BURIED STORIES: A HISTORICAL RECONSTRUCTION OF COMBUSTION PROCESSES AND INDUSTRIALIZATION IN LAKE BOTANISK, COPENHAGEN, DENMARK

A Thesis

by

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ABSTRACT

Lake Botanisk, a small isolated body of water that was once a part of the moat that surrounded Copenhagen, Denmark, has remained relatively undisturbed for four centuries. Due to this long undisturbed record and restricted watershed, its sediments serve as an excellent historical archive. The concentrations of various polycyclic aromatic hydrocarbons (PAHs), black carbon (BC), mercury (Hg), and lignin were measured in a sediment core from Lake Botanisk to assist with reconstruction of historical events for that region, including combustion associated with changes in fuel sources and industrial activities. Source diagnostic ratios indicate that PAHs were primarily derived from pyrogenic rather than petrogenic sources throughout the core. Marked increases in PAH concentrations during the pre-industrial era (<1860) trace major geopolitical events of that period (e.g. the bombing of Copenhagen by British Navy in late 1700s, and two major fires). The ratio of retene/(retene+chrysene) demonstrates that until ~1860, Copenhagen's combustion sources were dominated by wood burning. During these years, Hg and lignin concentrations in the lower core were strongly correlated, indicating that the primary vehicle for Hg input into the lake was via organic matter transport. After the lake was isolated from the moat in the early 1870's, Hg became more strongly correlated with pyrogenic PAHs, indicating that combustion byproducts entering the lake did so via atmospheric deposition. A significant rise in combustion-derived PAHs and BC was observed with the start of the Industrial Revolution, which corresponds to the start of coal imports in Denmark (1860s). The shift to coal consumption starting in 1860 leads to simultaneous increases in pyrogenic PAHs and isomer ratios (benzo[b]fluoranthene/benzo[k]fluoranthene) typical of coal usage.

Variations in PAH concentrations and ratios during the 20th Century track the shifts in energy sources (coal to oil, oil to natural gas), major political events such as the world wars, the Great Depression (1930), the oil embargo of 1970s (oil back to coal), and air quality standards and improvements in combustion technologies in recent decades (>1980s). Despite significant decreases in PAH, BC, and Hg since the early-20th century peak, levels still remain an order of magnitude above preindustrial values suggesting an impact from the growth in urban development.

DEDICATION

To my husband, Ryan:

Without your support over these last few years I would not have been able to accomplish what I have. You are the love of my life and I thank you for your constancy. I am so happy to be blessed with your presence every day.

To my family:

Mom & Dad – Thank you for raising me up in the way I should go. You have taught me that hard work should to be tackled with vigor and that there is satisfaction in a job well done, for that I am eternally grateful. I love you both so very much.

Alysha – You always have been, and you always will be my special little sister. Thank you for being the ray of sunshine that you are. I'm so proud of the intelligent and kind woman you are becoming.

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NOMENCLATURE

Anth	Anthracene
ASE	Accelerated solvent extractor
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BC	Black carbon
BeP	Benzo[e]pyrene
BghiP	Benzo[g,h,i]perylene
BkF	Benzo[k]fluoranthene
Chrys	Chrysene
DA	Dibenz[a,h]anthracene
Fl	Fluoranthene
GC-MS	Gas chromatography - mass spectrometry
HCl	Hydrochloric acid
HMW	High molecular weight
IP	Indeno[1,2,3-c,d]pyrene
Lead	Pb
LMW	Low molecular weight
LOP	Lignin oxidation products
MePhe	Methylphenanthrene
Mercury	Hg
NIST	National Institute of Standards and Technology
NRCC	National Research Council of Canada
PAH	Polycyclic aromatic hydrocarbon
Phe	Phenanthrene
Pyr	Pyrene
Ret	Retene

Sig8	The sum of lignin-derived constituents
SIM	Selective ion monitoring
SRM	Standard Reference Material
1,7-DMP	1,7-dimethylphenanthrene
2,6-DMP	2,6-dimethylphenanthrene

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

For centuries, mankind has relied upon the combustion of organic matter to provide heat, energy, safety, and a myriad of other uses. As time passed, populations grew larger, and technology evolved to include the combustion of fossil fuels, ushering a number of select nations into the Industrial Revolution. The increase in widespread combustion of coal and other fuels resulted in massive changes in air quality in the centers of industrialism. Perhaps the most well-known example of degraded air quality is that of London's Great Smog in 1952, when a dense fog trapped atmospheric contaminants at low altitudes for four days. The death toll from exposure to these contaminants was more than 3,000 people (Bell and Davis, 2001). This and other events led to the implementation of clean air policies within developed nations in order to improve air quality (Davis, 2002). Despite the trend towards improved air quality in developed nations, it is necessary to establish preindustrial baselines of a number of pyrogenic contaminants in order to assess the extent to which evaluate the extent to which these policies have been effective in returning their atmospheric emissions and depositions to their pre-industrial levels.

As such, it has become important to track the byproducts of combustion processes in order to fully assess the threat they pose to human health and to evaluate their life-cycle within the environment. Several studies have proposed the use of a continuum when characterizing combusted organic matter, or pyrogenic carbon (PyC) (Fig 1; Keiluweit et al., 2010; Masiello, 2004). This is due to the physical alterations that occur in the chemical structure of organic matter as it is burned. During combustion, organic matter is gradually changed from large and complex carbonaceous polymeric structures to microparticles via dehydration, aromatization, and aromatic condensation (Wiedemeier et al., 2014). Feedstocks have been shown to influence the resulting structure of PyC to a certain extent (McBeath and Smernik, 2009); however it has been found that combustion temperature tends to have a greater influence on the extent of aromaticity and aromatic condensation

in PyC. Lower combustion temperatures will result in the production of charred biomass and chars. These combustion temperatures (150 - 300ºC) cause lignocellulosic macropolymers in organic matter to dehydrate and fragment (Harvey et al., 2012; Keiluweit et al., 2010) . From approximately 350 - 500ºC, aromatization begins to occur, resulting in the formation of amorphous charcoals. From temperatures at approximately 600ºC and greater, further aromatic condensation of volatile organic carbon from the gaseous phase takes place, resulting in the formation of stacks of graphene, or soot (Harvey et al., 2012; Preston and Schmidt, 2006; Wurster et al., 2015).

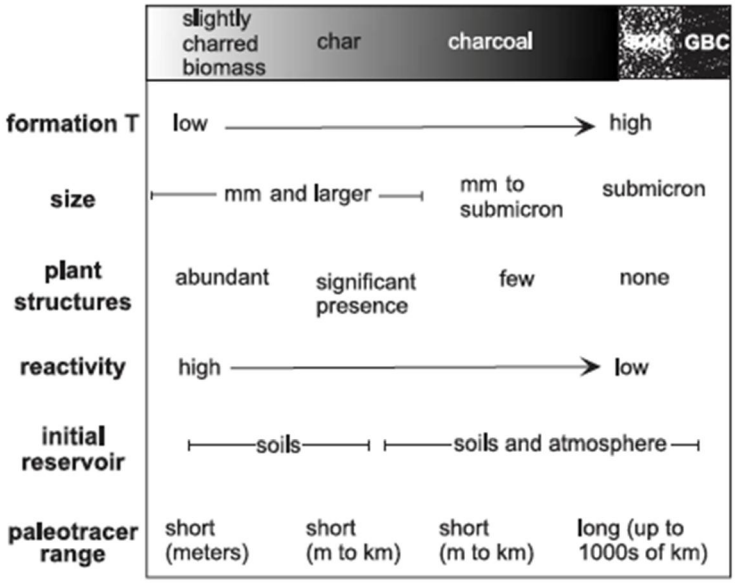

Figure 1. Black carbon combustion continuum as proposed by Masiello, 2004.

In particular, this study will focus on black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs), molecular contaminants which are emitted from the incomplete combustion or organic matter. BC is a general term that is often used to refer to the entire spectrum of PyC (Kuo et al., 2008; Masiello, 2004). However in this study, the term BC will be used to specifically discuss the constituents of the PyC continuum that are highly-condensed, highly aromatic, as well as biologically and thermally resistant. These

constituents are produced through high temperature combustion processes (> 600ºC) that tend to result in highly refractory soot particles which can be mobile in the atmosphere. Due to the fact that BC is produced at very high temperatures, studies have found that it can be used as an indicator of fossil fuel combustion and therefore a proxy for industrialization and urbanization (Ö Gustafsson and Gschwend, 1998; Louchouarn et al., 2007). Likewise, PAHs can be utilized in a similar manner, however they tend to be produced at intermediate to high temperatures (300-500ºC), with varying species being formed at different temperatures and from different fuels (Lima et al., 2005; McGrath et al., 2003). Because of these characteristics, identification of PAHs can clarify the sources of combustion-derived PyC in air samples, dirt or dust samples, sediment cores, and ice cores.

1.2 Sediment Cores and Previous Studies

Significant increases in concentrations of BC and PAHs in the environment and atmosphere in the last 100-150 years have been primarily associated with the rise of industrial activities and extensive urban development since the onset of the Industrial Revolution (Gustafsson and Gschwend, 1998; Gustafsson et al., 1996; Kuo et al., 2011; Laflamme and Hites, 1978b; Lima et al., 2005; Louchouarn et al., 2007). In the late 70's, Laflamme and Hites (1978) proposed measuring PAHs in sediment cores to study the historical fluxes of combustion by-products to urban centers vs. rural areas (Lima et al., 2005). Since that time, sediment cores have been used to analyze PAH and BC fluxes because they can provide relatively undisturbed historical records of atmospheric and/or water quality in specific areas (Elmquist et al., 2007; Kuo et al., 2011; Lima et al., 2005; Louchouarn et al., 2007).

In light of this, lakes that have existed in urban centers for a hundred years or more provide the opportunity to conduct a time-trend-analysis of the effects of, and changes in, anthropogenic combustion products due to large-scale changes from urbanization and industrialization (Louchouarn et al., 2007; MacFarlane and Gschwend, 1997; Wakeham et al., 2004). BC and PAH profiles in ancient sediments tend to be characterized by low

levels with rapid increases that reflect the occurrence of fires. In contrast, modern sediments have been found to contain significantly higher levels of BC which correspond to increased fossil fuel combustion (Kuo et al., 2011; Louchouarn et al., 2012). Further, changes in BC profiles throughout sediment cores have offered clues as to the shifts in regional fossil fuel usages (Griffin and Goldberg, 1981; Gustafsson and Gschwend, 1998; Kuo et al., 2011; Louchouarn et al., 2007) .

Similar studies have been conducted in areas such as the Hood Canal and Puget Sound in Washington (Wakeham et al., 2004; Kuo et al., 2011; Louchouarn et al., 2012), Aspvreten, Sweden (Elmquist et al., 2007), as well as Central Park Lake in New York City (Louchouarn et al., 2007; Yan et al., 2005). Not only do the results from these studies demonstrate that sediment cores are useful for the investigation of anthropogenic inputs of BC and PAHs, but they also help illustrate regional differences in the environmental impacts of urbanization and industrialization. In certain studies, BC and PAHs were found to be somewhat correlated (Gustafsson et al., 1996; Wakeham et al., 2004). As both of these byproducts are combustion derived, this is not fully unexpected, however the studies conducted in both Central Park and in Aspvreten found that BC and PAHs were decoupled from each other. While BC and PAHs may result from similar fuel sources, Louchouarn et al. (2007) demonstrated the impact that varying fuel sources, combustion temperatures, and sample site locations can have upon the resulting trends.

1.3 Objectives and Hypotheses

1.3.1 Broad Objective

The primary objective of this work was to reconstruct the history of anthropogenic contaminant inputs to the atmosphere of Copenhagen, Denmark, using a variety of chemical tracers in a geological archive that has been previously dated to an age of 400 years. In addition, this work sought to use chemical tracers to better constrain the geochronology beyond the limits afforded by the radiochronological methods used (^{137}Cs and ^{210}Pb).

1.3.2 Specific Objectives and Hypotheses

Objective 1

- To quantify the concentrations of combustion-derived byproducts such as PAHs and BC. Profiles and ratios will be used to clarify the source(s) of these contaminants:

  H1: The concentrations and ratios of pyrogenic PAHs and BC present in sediment layers will accurately characterize the history of combustion in Copenhagen over time.

  H2: The combustion sources identified by PAH signatures will correspond with known historical shifts in fuel sources (e.g. wood vs. coal vs. petroleum) and combustion technology.

  H3. As observed in other similar urban lakes, the concentrations of PAHs and BC following the start of the Industrial Revolution will be decoupled pointing to shifts in combustion technology and fuel sources.

Objective 2

- To quantify the concentration of lignin throughout the core in an effort to identify the depth of the core that corresponds to the years in which the moat was filled in:

  H3: Levels of lignin in the core will be elevated during the mid- to late 1800's in conjunction with the period when the moat was filled in.

Objective 3

- To quantify the concentration of Hg in the core and determine whether its presence is linked to the combustion of fossil fuels.

  H4: The Hg profile will reflect inputs primarily from the use of coal in Copenhagen, Denmark.

2. BACKGROUND

2.1 Black Carbon

A variety of concerns surround the emission of particulate BC into the atmosphere. Medically, BC has been found to cause pulmonary disease and asthma, primarily because the ultrafine particulates are not removed from the lungs by phagocytosis (Long et al., 2013). Additionally, the particles have the possibility to migrate throughout the body and accumulate in other tissues (Avakian et al., 2002). It is important to note, however, that a majority of studies on the health effects of BC do not clarify which portion of the PyC continuum is being studied, but rather use the term "BC" to refer to the entire atmospheric emission spectrum. As such, these studies may be confounding actual health effects of high temperature BC (Long et al., 2013; Gardiner and Tongeren, 2001), thus highlighting further the need for further clarification of the PyC spectrum. The presence of BC has been demonstrated in the atmosphere and urban topsoils (He and Zhang, 2009; Wang et al., 2012) of industrialized nations and is therefore a concern with respect to human exposure (McBeath and Smernik, 2009)

With respect to environmental concerns, while BC may be subject to photodegredation in the atmosphere, the large degree of aromatic condensation in the particles makes BC less reactive and therefore more inert in most aquatic and terrestrial environments. Because of this, the production of BC is believed to contribute to the earth's slow-cycling carbon pool. It is also of concern due to its highly refractory nature which, scatters and absorbs incoming solar radiation, thus implicating BC in radiative forcing and warming of surface temperatures (Flanner et al., 2007; Hansen and Nazarenko, 2004). Furthermore, accumulation of BC on surface snow at the poles has been found to have altered the albedo of these regions, potentially aiding the speed at which snowmelt progresses (Penner et al., 1993). In particular, concentrations ranging from 5 – 300 parts per billion by weight of snow have been measured in the Arctic while lower concentrations have been observed in the Antarctic (Hansen and Nazarenko, 2004).

Such widespread occurrence of BC has been believed to illustrate its ability to be transported for long ranges depending upon environmental conditions (Parungo et al., 1994; Louchouarn et al., 2007), a consequence of its ability to remain in the atmosphere for up to a few weeks. However, despite the global nature and distribution of BC, studies have illustrated substantial regional differences in BC trends (Stout and Emsbo-Mattingly, 2008). It is likely that the global heterogeneity of BC distribution is due to varying trends in fuel use and combustion history from region to region. As such, there is a need for greater clarification of BC depositional trends and sources. Furthermore, a comparison of the historical records of regional atmospheric BC releases with historical temperature changes can elucidate the extent to which BC has affected temperature changes (Hansen and Nazarenko, 2004; Highwood and Kinnersley, 2006; Jacobson, 2004; Krishnan and Ramanathan, 2002).

With such a list of concerns surrounding the emission of BC, it is not surprising that policy-makers such as the EPA have made efforts in the last few years to monitor and reduce the rate at which BC is emitted to the atmosphere[1]. The United Nations Environment Program (UNEP) has proposed regulations regarding emissions from vehicles, cooking and heating stoves, industrial restrictions on kilns, shafts and coke ovens, and the burning of fields and agricultural waste (United Nations Environment Programme and World Meteorological Association, 2011). The 28th executive session of the UNEP stated that they expect BC emissions in UNEP nations to be reduced by one third by 2020 primarily as a result of emission regulations in the transportation section (Ad-Hoc Expert Group on Black Carbon, 2010). While these efforts are certainly laudable, further clarification to the specific sources of BC regionally would significantly aid decision makers with regards to policies regarding emission regulations.

[1] More information about these policies is available on the EPA website

2.2 Polycyclic Aromatic Hydrocarbons

Unlike BC, PAHs are derived from both petrogenic as well as pyrogenic sources. Petrogenic PAHs are formed via long-term maturation of organic matter, often under pressure, as is seen in petroleum and diagenesis of organic matter in anoxic sediments (Killops and Killops, 2005; Laflamme and Hites, 1978a-b). These PAHs, and those produced via combustion at low temperatures are comprised predominantly of low-molecular weight units (2-4 aromatic rings) and enriched in alkyl groups. In contrast, pyrogenic PAHs, particularly those produced at higher temperatures, contain a much higher proportion of high-molecular weight constituents (4-6 aromatic rings) and are almost completely devoid of alkyl functional groups (Mostert et al., 2010). PAHs tend to be produced at temperatures ranging from 300 - 500ºC, thus they are found at intermediate combustion temperatures within the PyC continuum (Fig 1).

The primary issue with PAHs is that many have been shown to have both mutagenic as well as carcinogenic effects and are therefore characterized as primary contaminants of concern (Bostrom et al., 2002). It is common for studies to include PAHs under the category of BC thus causing confusion about which constituents of the PyC continuum are responsible for varying medical ailments. Furthermore, certain studies have indicated that BC may sorb PAHs, thus acting as a carrier phase (Brändli et al., 2008; Long et al., 2013). However, it has not been clarified whether the health effects of BC-sorbed PAHs demonstrate primarily the inflammation causing and cardiovascular properties of BC, or the mutagenic and carcinogenic properties of PAHs.

Typically PAH concentrations are used to indicate products of anthropogenic combustion processes, however they can also be produced during natural combustion events, such as forest fires (A. Dvorská et al., 2011; Tobiszewski and Namieśnik, 2012). PAHs are particularly useful in that the multiple species, which are emitted as a mixture, can be used for diagnostic purposes by investigating the proportional concentration ratios in which they are found in the environment (Jr et al., 2003; Laflamme and Hites, 1978a, 1978b; Yan et al., 2005; Yunker and Macdonald, 2003). Diagnostic ratios are developed for

sources by investigating the relative concentrations of alkyl homologues, isomer ratios, or molecular weight proportions that are produced during combustion and vary with substrates and formation pathways.

Several studies have monitored the concentrations of PAHs in atmospheric particles as a measure of air quality. However, these approaches are limited in their duration and provide little information on air quality beyond the sampling period. In particular, historical reconstructions in periods prior to regular monitoring need to rely on appropriate environmental archives, in which chronology is well constrained. Archives with long term depositional records, such as sediment and ice cores have been used to establish historical trends for contaminants such as PAHs. While some combustion-derived PAHs are dispersed over long distances via atmospheric transport most are deposited near their emission source (Yan et al., 2005), further highlighting the utility of using sediment cores from urban lakes and coastal environments to reconstruct combustion trends (Elmquist et al., 2007; Kuo et al., 2011; Lima et al., 2003; Louchouarn et al., 2012, 2007; Wakeham et al., 2004). PAH diagnostic ratios are typically employed in such studies for source apportionment. (Zhang et al., 2008; Yan et al., 2005).

It is important to note that some have questioned the accuracy of utilizing diagnostic ratios for source apportionment, particularly with regards to PAHs in sites that are far from sources (Dvorská et al., 2011). This is due to the fact that PAHs are subject to photodegradation as well as varying reactivity in the atmosphere with regards to changing seasons, thus making relative concentrations of PAHs non-conservative between the source and deposition sites (Yamasaki et al., 1982). Additionally, in aquatic environments some PAHs can partition differently between the dissolved and the particulate phase, which could confound the accuracy of studies that are conducted on sediment cores (Brandenberger et al., 2008; Louchouarn et al., 2012). Because of this, studies that use isomer ratios (with similar physical properties) and can directly compare PAH ratios to known historical events and combustion sources will significantly aid in the clarification of the accuracy of utilizing such diagnostic ratios for source apportionment.

2.3 Heavy Metals

In addition to the release of PAHs and BC, combustion processes can also be a significant source of heavy metals such as Hg and Pb to the environment (Louchouarn et al., 2012; Lucotte et al., 1995; Yudovich and Ketris, 2005). As with BC and PAHs, heavy metals found in sediment cores can be used to reconstruct historical emissions that reflect the impact of urbanization on atmospheric and aquatic environments (Kuo et al., 2011; Louchouarn et al., 2012). Pb emissions in the 20th century have largely been influenced by the use of tetraethyl lead in gasoline. Although the EU began to limit Pb additives placed in gasoline in the late 1980's, it wasn't until the early 2000's that leaded gasoline was significantly eliminated from European countries as a result of the 1998 Aarhus Treaty (Fig 2; Pacyna et al., 2009; V. H. Storch et al., 2003). In Denmark, emissions were found to have decreased by two orders of magnitude over 30 years (from ~1,600 to16 tonnes yr^{-1} between the years 1965 and 1995; Pacyna et al., 2001). Aerosol particulate Pb emissions tend to have an atmospheric residence time of 6-12 days (submicron fraction) which constrains Pb to relatively smaller regions when compared to other heavy metals like Hg. This can be observed by the wide variety of Pb emissions levels observed across European countries over the last few decades (Pacyna et al., 2001).

Sources of anthropogenic Hg in the atmosphere can be derived from the incineration of various forms of waste including industrial, residential, and human sludge. Other emission sources include the iron and steel industry, gold production, as well as the chlor-alkali industry (Louchouarn and Lucotte, 1998a; Pacyna et al., 2008). However, the greatest portion of the Hg emitted worldwide presently can be attributed to the combustion of fossil fuels, with the majority being produced by coal, which is commonly used to produce electricity. In contrast to Pb emissions, elemental Hg has an extended tropospheric residence time of about one year, allowing for widespread distribution of this form of Hg globally (Heyvaert et al., 2000). Hg directly emitted from coal combustion in electricity plants is typically elemental, but will react with other flue gas constituents as it travels through the stack. These reactions produce compounds like mercuric chloride ($HgCl_2$) and

mercury (II) oxide (HgO) which tend to be less stable than elemental mercury and will therefore have a shorter atmospheric residence time and tend to fall out of the local atmosphere in which they were emitted.(Carpi, 1997; Hall et al., 1990).

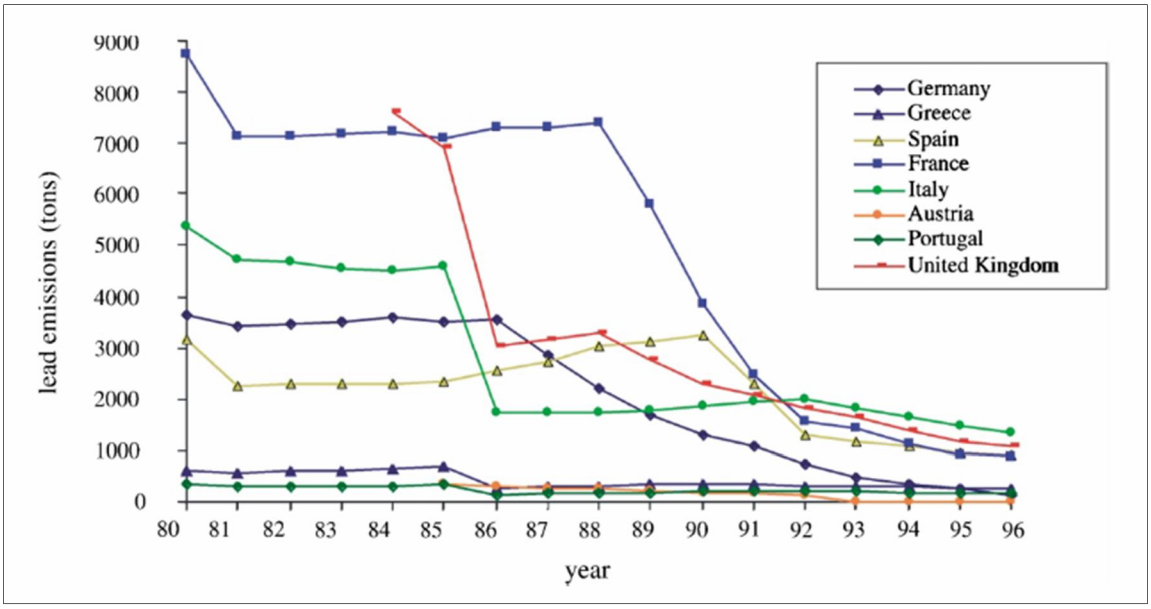

Figure 2. Data sets on lead emissions in 12 European Union nations (Eurostat, 1998; Storch et al., 2003).

Flue gas desulfurization was invented in the early 1930's, and has been found to be effective at removing not only sulfur dioxide, but also Hg. The combined use of flue gas desulfurization and electrostatic precipitators were found to have contributed to the reduction of Hg emissions in Western Europe since the 1980's (Pacyna et al., 2009; Storch et al., 2003). As such, it is expected that Hg levels found in sediment cores from this region in Europe would be seen do decrease around this time (Fig 3). Additionally, fuel sources have been altered over the years to include a greater proportion of oil and petroleum, thus contributing to a general reduction in atmospheric Hg.

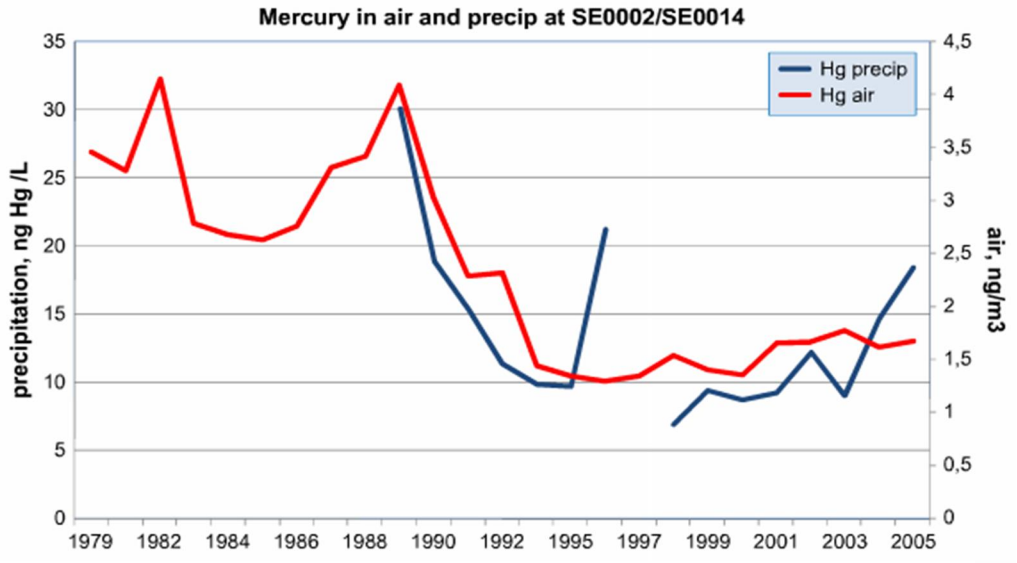

Figure 3. Hg concentrations in air and precipitation in Western Europe from 1979 – 2005 (Pacyna et al., 2009).

Due to the known toxicity of both Pb and Hg, environmental policies have been wise to implement regulations on known point sources. Studies conducted since the 1970's have documented the general decrease in emissions of Pb and Hg at various stations in Europe. Up to 85% reductions in Pb were observed in different countries, presumably due to the limiting of leaded gasoline. Similar decreases were observed in Hg levels in Sweden (Pacyna et al., 2009). However these trends were only measured over the course of a few decades, therefore providing little information about Pb and Hg emissions prior to the 1970's. As is the case with BC and PAHs, policies have been formed on estimates of levels of these contaminants that are presumed to be acceptable to human health. However there is no data available to indicate what atmospheric levels were like prior to heavy coal and gasoline usage.

2.4 Lignin Oxidation Products

The term lignin represents a family of aromatic biomacromolecules that form one of the major components found in the structural units of vascular plants (Sarkanen and Ludwig, 1971). Due to the fact that lignin is found exclusively in vascular plants which are

indigenous to land, many studies have utilized lignin oxidation products (LOPs) as geochemical tracers for inputs of terrestrial organic material into aquatic systems and sediments (Gordon and Goñi, 2003; Goñi et al., 1998; Louchouarn et al., 1999; Louchouarn et al., 1997). Much like PAH ratios are used to determine combustion sources, the phenolic ratios of lignin are used to identify specific vegetation sources that have contributed to lignin input into these aquatic systems (Amon et al., 2012; Hedges et al., 2000, 1988; Louchouarn et al., 2010).

In addition to clarifying the types of vegetative inputs into aquatic systems, lignin concentrations can be utilized to identify pulse events. Floods in particular have been found to increase the quantity of organic carbon and lignin within aquatic systems due to the mobilization of soils and sediments (Dalzell et al., 2005; Kuo et al., 2014). Anthropogenic contributions of lignin to aquatic environments have been documented in the form of effluents from pulp and paper mills as well as activity in the logging industries (Louchouarn et al., 1999). These examples highlight the ability to utilize changing lignin concentrations throughout sediment cores to characterize the disturbances and fluxes of organic matter to aquatic systems. For instance, if historical records indicate the occurrence of a flood event in a region, lignin concentrations and/or quality in the corresponding sediment layer should shift accordingly. As such, lignin concentrations could theoretically be used to clarify sediment chronology if accurate historical records were available.

2.5 Study Site and Research Objectives

Lake Botanisk provides a unique opportunity to study long term combustion-derived atmospheric deposition due to its prolonged existence (~400 years) in an urban environment. Originally, the lake was situated in the northwestern portion of a moat that surrounded the city in the mid 1600's and was connected on the east and west with a bay of the Baltic Sea. During the years 1872 - 1874, portions of the moat were filled in leaving Botanisk and several other sections of the moat as isolated lakes (Fig 4). Since then, Lake Botanisk has had no incoming or exiting streams. Because of this, the lake has functioned

as a trap for atmospheric deposition, thus making it an ideal study site for historic depositional reconstruction. The purpose of this study was to reconstruct the history of anthropogenic contaminant inputs to the atmosphere of Copenhagen, Denmark, using a variety of chemical tracers in a geological archive going back 400 years. Additionally, multiple chemical tracers were used to better constrain the geochronology beyond the limits afforded by radiochronological methods (^{137}Cs and ^{210}Pb).

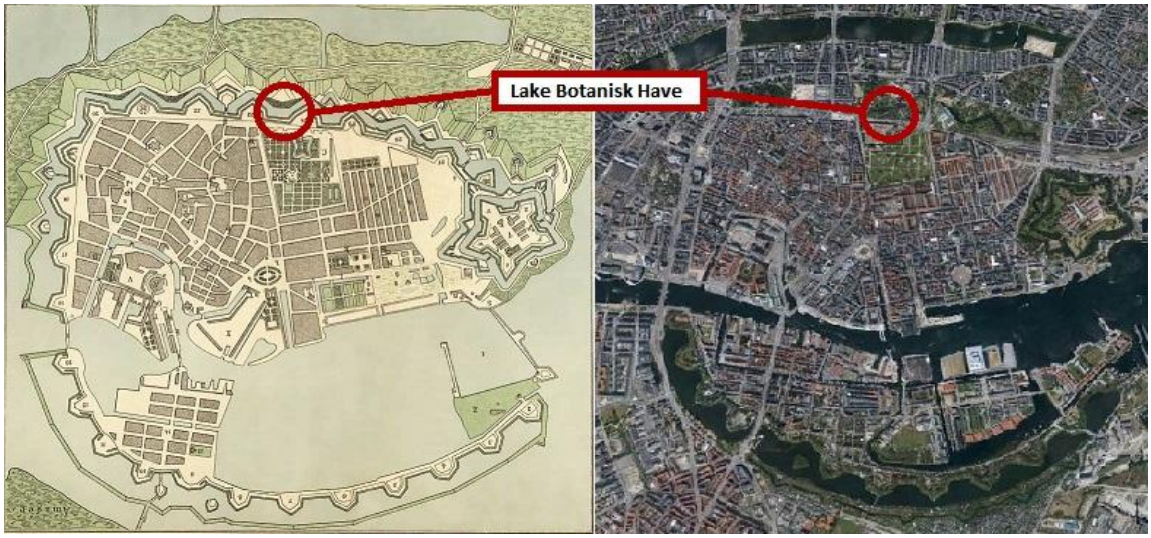

Figure 4. Maps of Copenhagen, Denmark. Lake Botanisk as part of the moat surrounding Copenhagen in 1728 (Left) (Arnøldt, 1728). Lake Botanisk as seen today (Right) (Google Earth, 2014)

Specific PAH diagnostic ratios were used to analyze sediment layers and trace the source(s) and quantity of combustion changes over time. Results from this analysis were then compared with historical combustion data and other contaminants (e.g. heavy metals), in order to corroborate the accuracy of utilizing PAHs to characterize combustion sources. In addition, BC concentrations were also quantified throughout the core to clarify the inputs of high temperature combustion byproducts to the airshed of Copenhagen. It was hypothesized that the combustion sources identified by PAH signatures as well as the trend of BC in the core would correspond with records of historical shifts in combustion technology and fuel sources (e.g. wood vs. coal vs. petroleum).

In addition to PAH and BC analyses, the lignin concentrations in the core were quantified; this analysis was included because of its potential to track any significant changes in the sources, quality, and quantity of terrigenous organic matter (OM) entering the lake over the years. It is likely that, during the process of filling in the northern portions of the moat, a great deal of perturbation to sediment inputs took place. The soil used as fill material certainly contained woody plant matter which would either elevate the levels of lignin found within the sediment or change its proportion to total OM. In light of this, any significant shifts in lignin concentrations around this time, either absolute (to sediment) or relative (to OM), could help better constrain the chronology of the lower core. This was particularly helpful as the dating method used on the Botanisk core was based radiochronologically (^{137}Cs and ^{210}Pb), and is therefore limited to 100-200 years of reconstruction (Blais et al., 1994; Davis et al., 1984). Furthermore, studies have found that organic matter can act as a carrier phase for Hg (Louchouarn et al., 1998; Smith and Loring, 1981). Depending upon the types of organic carbon found in the Botanisk core, an analysis of the lignin concentrations sediments may help clarify inputs of Hg into the lake.

Records from the Natural History Museum of Denmark show an increase in the importation of coal to Denmark beginning around 1860 and reaching a high in the 1990's during the OPEC oil embargo (Fig 5). Fluctuations in the importation rates between these years coincide with known historical events such as the first and second World Wars, as well as the OPEC Oil Embargo. If Hg concentrations within the core are primarily due to the combustion of fossil fuels, then the expected trend would mirror those of the coal and oil importation into Denmark. In light of this, the Hg concentrations might be utilized to determine whether PAH concentrations correlate primarily with coal usage (Yudovich and Ketris, 2005).

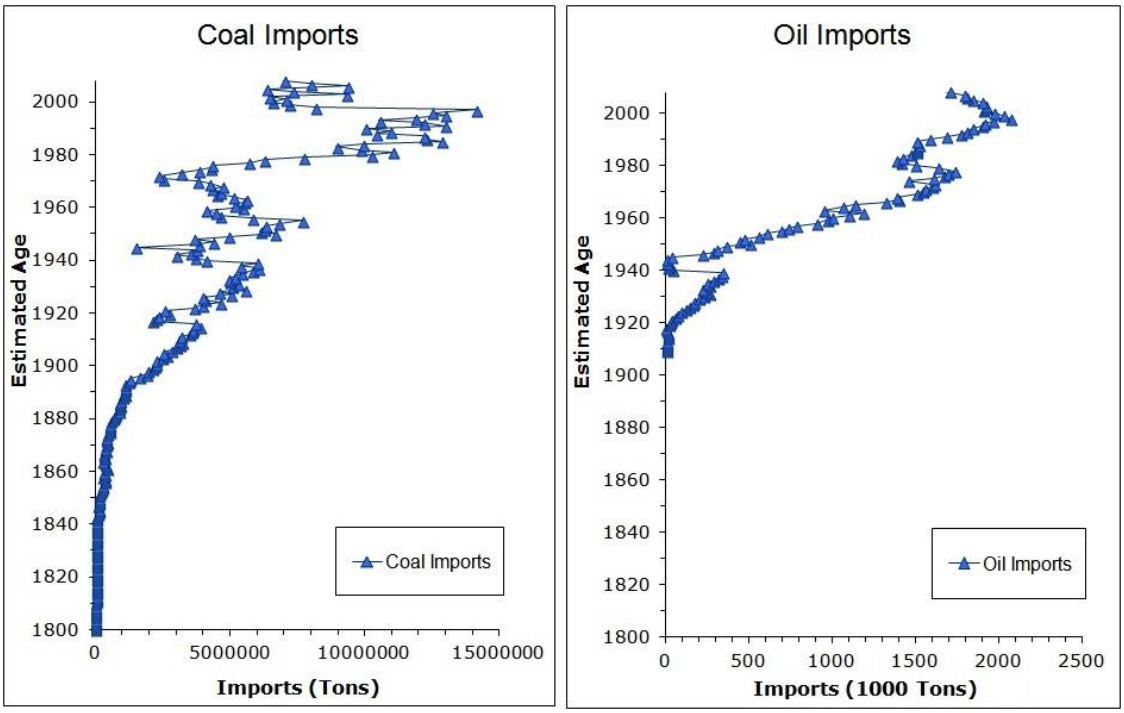

Figure 5. Coal and oil importation into Denmark from the year 1800 to present.

3. METHODOLOGY

3.1 Site Information and Sample Collection

Sediment cores were sampled from Lake Botanisk in Copenhagen's Botanical Garden in the winter of 2011. The cores (150 cm long) were collected through the ice and were sub-sectioned every cm depth in the lab after retrieval. Sediment intervals were then freeze-dried and sent to the lab at Texas A&M University at Galveston. Each sediment sub-sample was then homogenized using a ball mill prior to any analysis. The sediments were dated by the National History Museum of Denmark and the Geological Survey of Denmark and Greenland using ^{210}Pb and ^{137}Cs dating methods for the recent 100 years. To constrain the lower portions of the core, synchronization points were identified as visible color changes that appeared in all of the sediment cores taken from the lake. These points were then dated using known historical events and the sedimentation rates were determined between the points.

3.2 Elemental Analysis

Organic carbon (OC) and total nitrogen (TN) concentrations were determined for all sediment samples that were to be used for the further analysis. Dried sediments were first acidified twice for 30 minutes in 1N HCl to remove any carbonates in the samples. The sediments were then rinsed with water, centrifuged, and the water was pipetted off before the sediments were dried thoroughly at 60ºC. The dried sediments were then homogenized with a mortar and pestle and then weighed out into tin capsules for analysis using a Costech elemental analyzer. Standard reference materials (NIST, SRM 1941b) and replicates were also included with each set of samples to ensure accuracy. The measured %OC and %TN of the SRMs (3.17 and 0.27% respectively) fell within the certified range (2.99 ± 0.24% and variability of the certified values and <0.5% respectively). The coefficient of variation (CV) for both analyses was 6% and 7% respectively.

3.3 PAH Analysis

Approximately 1g of homogenized sediment was spiked with PAH surrogate standards (d10-phenanthrene and d12-chrysene) and extracted using a pressurized fluid extraction in an accelerated solvent extractor (Dionex ASE 200) with dichloromethane (DCM) as a solvent. The extraction was carried out at a pressure of 10.3 MPa and a temperature of 100°C. The resulting extracts were treated overnight with pre-cleaned and activated granular Cu to remove the elemental sulfur. Using a RapidVap solvent exchanger (Labconco), the extracts were then concentrated and solvent-exchanged into approximately 2 mL of hexane. Following purification using alumina column chromatography and approximately 35 mL of petroleum ether as an eluent, the extracts were again concentrated and solvent exchanged into 1 mL hexane before being transferred into glass vials for storage (Fig 6). GC-internal standards (d10-fluorene and d12-benzo[a]pyrene) were then added to the final concentrated extracts prior to gas chromatography mass spectrometry (GC-MS) analysis (Fig 6). One sample of a standard reference material (NIST, SRM 1944) and a blank were also included in each run to test for accuracy of the method.

Figure 6. Equipment used for PAH analysis. Alumina columns with eluent (left) and the GC/MS used for PAH quantification (right).

Separation and quantification of PAHs were performed using gas chromatography–mass spectrometry (GC/MS) with a Varian Ion Trap 3800/4000 system fitted with a fused silica column (VF 5MS, 30 m x 0.25 mm i.d., 0.25 μm film thickness; Varian Inc.). Each sample was injected under splitless mode, into a deactivated glass liner inserted into the GC injection port and using Helium as the carrier gas (~ 1.0 mL min^{-1}). The GC oven was programmed from 60°C (with a 2 min initial delay) to 150°C using a temperature ramp rate of 15°C/min. This was followed by an increase to 220 °C at a rate of 5°C/min and a third increase to 300°C at a rate of 10°C/min. (held 10 min). The GC injector and GC/MS interface were maintained at 300°C and 280°C, respectively. The mass spectrometer was operated in the electron ionization mode (EI, 70 eV) using selective ionization mode (SIM). Method detection limits for target PAHs have been previously found by Brandenburger et al. (2010) to average 1.0 ± 1.6 ng/g (SI Table 1). Compound identification was performed using GC retention times and by comparing mass spectra with those of commercially available standards. The following compounds were included in the pyrogenic PAHs: pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluroanthene (BbF), benzo[k]fluorathene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IP), dibenz[a,h]anthracene (DA), and benzo[g,h,i]perylene (Bghi). All blanks yielded non-detectable levels for the PAHs of interest. The PAHs from the SRMs fell within the ± 20% variability of the certified values.

Table 1. Method detection limits for PAHs.

Compound	MDL (ng/g)
Naphthalene	1.95
Biphenyl	2.50
Acenaphthylene	0.73
Acenaphthene	1.01
Fluorene	0.69
1-Methylfluorene	0.69
Dibenzothiophene	0.41
Phenanthrene	8.00
Anthracene	0.37
1-Methylphenanthrene	0.37
3,6-Dimethylphenanthrene	0.00
2,6-Dimethylphenanthrene	0.48
1,7-Dimethylphenanthrene	0.32
Fluoranthene	0.83
Pyrene	0.54
Retene	0.35
Benzo(a)anthracene	0.38
Chrysene	0.52
Benzo(b)fluoranthene	0.99
Benzo(k)fluoranthene	0.47
Benzo(a)pyrene	0.32
Perylene	0.04
Indeno(1,2,3-c,d)pyrene	0.56
Dibenz(a,h)anthracene	0.19
Benzo(g,h,i)perylene	0.72

3.4 GBC Analysis

To measure the BC contained in the core samples, graphite black carbon (GBC) analysis was employed to identify BC produced at high temperature and containing higher quantities of soot. GBC analysis is a chemo-thermal oxidation process by which the production of charred labile organic matter during treatment is minimized by demineralization, hydrolysis, and finally thermal treatment for 24 hours (Masiello, 2004). Mass loss is a potential drawback to this method (Kuo et al., 2011), however this was accounted for by treating more sample than was needed for the final CHN analysis. Additionally, the samples were weighed prior to and after treatment in their vials to ensure that any losses were accurately accounted for. Approximately 0.4 g of sediment were used for each sample, however this amount was adjusted upward, depending upon the percentage lost. Standard reference materials (NIST 1941b) were included along with the

analysis of the sediment samples to ensure quality control and estimate loss. Samples were first treated twice with 3mL of a 1N HCl solution for a duration of 1 hour each. This ensured full removal of carbonates and salts within the samples. The remaining sediment was separated from the liquid using centrifugation at a speed of 3000 rpm for approximately 20 minutes. The samples were then transferred to PTFE tubes and remained in these tubes for the duration of the treatments. To remove silicate minerals from the sediments, the samples were then treated with a mixture of 1N HCl and 10% Hydrofluoric acid (HF) for 12 hours at room temperature; this step was repeated twice to ensure full demineralization. To remove the hydrolysable organic material (HOM), the samples were then treated with trifluoroacetic acid (TFA) that had been purged with Ar. The TFA treatments were administered at 100ºC in increasing concentrations and durations: 2N for 3 hours, 4N for 18 hours, and 6N for 18 hours. The samples were treated for 24 hours with 6N HCl at 100ºC to completely remove any HOM. The samples were then rinsed with pure water and placed in a 60ºC oven until dry. Finally, the sediment samples were weighed into silver capsules (two capsules were stacked to avoid tearing) and combusted at 375ºC for 24 hours to remove all non-soot BC. The GBC content was then analyzed in a CHN elemental analyzer to determine the amount of carbon remaining in the samples. It is important to note that this remaining carbon consists of the highly condensed BC that is thermally stable.

3.5 Mercury Analysis

Hg content was measured for the entire core by a Direct Mercury Analyzer (DMA-80, Milestrone). Samples did not need pre-treatment as the DMA-80 detects the total Hg content of samples by degrading the sample thermally before oxidizing it. An Hg amalgamator then collects the volatilized Hg from decomposition products (Maggi et al., 2009), after which the Hg can be quantified using atomic absorption spectrometry. Standard reference materials (NRCC, MESS-3, Marine sediment; NIST 2702 Inorganics in Marine Sediment; and NRCC, PACS-2 Marine sediment) were included approximately every 10 samples to ensure that the DMA-80 was calibrated properly and reporting

accurate measurements. Replicates were also included periodically to indicate reproducibility. The Hg from the SRM's fell within ± 1.5% of the certified values for the MESS-3, ± 6.4% of the certified values for the NIST 2702, and ± 15.5% of the certified values for PACS-2. The mean analytical variability from replicates was 6.3 ± 4.7%.

3.6 Lignin Quantification

Lignin concentrations were analyzed using the method developed by Hedges & Ertel (1982), with modifications according to Louchouarn et al. (Louchouarn et al. 2010) and Norwood et al. (Norwood et al. 2013). Sediment weights were determined by using the OC percentages found in the elemental analysis to ensure at least 3 mg of OC per sample; the sediment was then placed into stainless steel reaction vessels (3 mL; Prime Focus Inc.) containing ferrous ammonium sulfate ($(NH_4)_2FE(SO_4)_2 \cdot 6H_2O$), cupric oxide (CuO) and oxygen free sodium hydroxide (NaOH). To verify accuracy, a NIST standard reference material (SRM 1941B) was included in each run of sediment samples. The samples were then purged with Argon gas to remove any remaining oxygen and the vessels were then placed inside a GC oven and subjected to thermal oxidation for 150 minutes at a temperature of 154°C. After oxidation, each of the samples was spiked with 50µL of 250 ng/µL concentration d-7 cinnamic acid, a surrogate standard. The vessels were then centrifuged to separate the sediment from the liquid fraction before decanting the liquid fraction and resuspending the sediment in 1N NaOH; a total of three liquid fractions were collected. The samples were then acidified with 6N HCl to a pH of approximately 1 or less. Three aliquots of 3mL of ethyl acetate were then sequentially added to the acidified samples to extract the reactive fraction; samples were vortexed each time to ensure complete extraction. To remove any residual water from the extracts, the samples were treated with Na_2SO_4 and then fully dried using a LabConco™ solvent concentrator. The oxidation products were then resuspended in 400µL of pyridine, then diluted further by removing a 50µL aliquot of the LOP products and combining them with 200µL pyridine. 50µL of each sample was then placed into a 250µL glass autosampler insert and then derivatized by adding 50µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)

containing 1% trimethylchlorosilane (TMCS; Supelco, PA, USA), followed by heating in a well block heater at 75°C for 30 minutes under normal atmospheric conditions. Within a few hours after derivatization, the samples were injected into a GCMS fitted with a Varian Ion trap and a fused silica column for analysis. Duplicates and standard reference materials were included with each set of samples that was analyzed in order to monitor accuracy and loss. GC-internal standards were also included in each run to help calculate recovery. The GCMS analysis was done in full scan mode and lignin phenol identification was performed using relative response factors (Louchouarn et al., 2010). Sig8 values for SRM's averaged 0.16 ± 0.03 mg g^{-1} and the mean analytical variability of Sig8 values for replicates was <15%.

4. BURIED STORIES: AN HISTORICAL RECONSTRUCTION OF COMBUSTION PROCESSES AND INDUSTRIALIZATION IN LAKE BOTANISK, COPENHAGEN, DENMARK

4.1 Overview

Concentrations of polycyclic aromatic hydrocarbons (PAHs), black carbon (BC), mercury (Hg), and lignin were measured in a sediment core from Lake Botanisk, Copenhagen, to reconstruct historical inputs of contaminants over four centuries. Source diagnostic ratios indicate that PAHs were primarily from pyrogenic sources and that until ~1860, Copenhagen was dominated by wood burning. Marked peaks in PAH concentrations during the pre-industrial era (<1860) trace major geopolitical events of that period (e.g. the bombing of Copenhagen). A significant rise in coal importation, combustion-derived PAHs, and BC was observed with the start of the Industrial Revolution (1860). During the 20th Century, variations in PAH concentrations and ratios track the shifts in energy sources, major political events such as the oil embargo of 1970, and implementation of air quality standards and improvements to combustion technology. Hg and lignin concentrations before 1870 were strongly correlated, indicating that the primary vehicle for Hg inputs into the lake was through organic matter transport via surface runoff. After Botanisk was closed off from the moat the 1870's, Hg was predominantly derived from coal combustion and atmospheric deposition. Despite recent decreases in PAH, BC, and Hg concentrations, levels remain 10-fold above preindustrial values suggesting an impact from industrial activities.

4.2 Introduction

The large-scale increase in the combustion of coal in the mid to late 1800's in Western Europe and North America that helped fuel the Industrial Revolution, resulted in massive alterations to air quality in industrialized cities (Ma et al., 2014; Vane and Chenery, 2011). Massive catastrophic events like London's Great Smog in 1952 (Bell and Davis, 2001) were catalysts for the implementation of policies regarding emissions within developed nations (Davis 2002). Inefficient combustion processes, such as the burning of wood and coal, are known to be major contributers of contaminants that are derived from incomplete combustion, such as black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs). During incomplete combustion, organic matter undergoes several transformation, some of which lead to a series of combustion byproducts, also called pyrogenic carbon (PyC). PyC is a generic term that has evolved in recent decades into a *continuum* model, which describes combustion byproducts ranging from slightly charred materials that retain information about the original structure of the parent material, to highly condensed and refractory soot (Keiluweit et al., 2010; Kuo et al., 2008; Masiello, 2004; Preston and Schmidt, 2006).

Simple particle size differentiation between char and soot has recently been augmented with methods employing optical, physical, chemical, and/or thermal treatments to separate non-combustion organic carbon (OC) from PyC (Hammes et al., 2007). Recent efforts to characterize changes that occur in organic matter during combustion (Harvey et al., 2012; Keiluweit et al., 2010; Schneider et al., 2010) have led to the refinement of the knowledge of PyC structure. Molecular changes in the original feedstocks evolve from initial fragmentation of macropolymers in the original fuel ("transition" charcoals) at low temperatures (200 - 350ºC), to an increased proportion of small aromatic clusters ("amorphous" charcoals) at medium temperatures (400 - 600ºC), to a high degree of condensation into larger graphene stacks ("turbostatic" charcoals) at high temperatures (>600ºC)

While BC is a general term that is often used to refer to the entire PyC continuum (Kuo et al., 2008; Masiello, 2004), this study will specifically use the term to refer to the highly-condensed, highly aromatic, and thermally resistant molecular consitutents that are produced via high temperature combustion processes (>600ºC). Such high temperature combustion tends to result in soot particles which are highly refractory and can be transported for long ranges within the atmosphere (Streets et al., 2001). The high temperatures at which BC is produced serves as an indicator of fossil fuel combustion, and as an extension, a proxy for industrialization (Gustafsson and Gschwend, 1998a; Kuo et al., 2011; Louchouarn et al., 2007). In a similar manner, PAHs can be used to discriminate sources of PyC due to the fact that unique molecular species and the degree of alkylation are related to sources and/or production conditions (petrogenic vs. pyrogenic sources, combustion temperatures, varying feedstocks, etc. (Lima et al., 2005; Tobiszewski and Namieśnik, 2012; Yunker and Macdonald, 2003; Yunker et al., 2002)).

Increases in environmental and atmospheric BC and PAH concentrations since the mid 1800's have been primarily associated with the onset of the Industrial Revolution and extensive urban development (Elmquist et al., 2007; Gustafsson and Gschwend, 1998; Gustafsson et al., 1996; Lima et al., 2003). In order to better understand the impact that such major combustion events have had on historical air quality, some studies have utilized "sentinel" archives that have existed for decades or longer, such as ice and sediment cores, to forensically reconstruct anthropogenic inputs to ecosystems (Kuo et al., 2011; Louchouarn et al., 2007). In particular, PAHs measured in sediment cores have been used to study the historical inputs and fluxes of anthropogenic combustion byproducts in urban and rural regions, thus reflecting air and water quality throughout history (Kuo et al. 2011; Laflamme and Hites, 1978b; Lima et al., 2005, 2003; Louchouarn et al. 2007; Elmquist et al. 2007).

In addition to the release of PAHs and BC, combustion processes can release heavy metals such as Hg and Pb (Louchouarn et al., 2012; Lucotte et al., 1995; Ma et al., 2014; Vane and Chenery, 2011; Y. Yudovich and Ketris, 2005). Sources of anthropogenic Hg in the

atmosphere can be attributed to incineration of various forms of waste including industrial, residential, and human sludge. Other emission sources include the iron and steel industry, gold production, as well as the chlor-alkali industry (Louchouarn and Lucotte, 1998a; Pacyna et al., 2008). However, the greatest portion of the atmospheric Hg emissions worldwide can be attributed to the combustion of coal, which is commonly used to produce electricity (Pacyna et al., 2006; Yudovich and Ketris 2005). As with BC and PAHs, heavy metals found in sediment cores can be used to reconstruct historical emissions that reflect the impact of urbanization and industrialization on aquatic environments (Kuo et al. 2011).

Sediment cores taken from lakes that have existed in centers of urban and industrial activity for over a hundred years allow for a time-trend-analysis of the effects that changing anthropogenic combustion processes have had on atmospheric levels due to large-scale industrialization and urbanization (Louchouarn et al., 2007; MacFarlane and Gschwend, 1997; Wakeham et al., 2004). Lake Botanisk in Copenhagen, Denmark provides an excellent opportunity to investigate historical trends in atmospheric deposition of combustion-derived contaminants in an urban environment due to its existance throughout the city's development over the last 400 years. The lake was originally included in the northwestern portion of a moat that was built in the mid 1600's and surrounded the entire city. It was connected on the east and west to the Baltic Sea. As the city developed, portions of the northern moat were filled in to allow for expansion. This construction took place in the years 1872 - 1874, and several sections of the moat were left as isolated lakes, Lake Botanisk included. Since then, Lake Botanisk has had no major incoming or exiting streams, although a small trench was built in the 1600's that connected a northern lake (Sortedam) with the moat near Botanisk in an attempt to supply the moat with a source of fresh water. Because of the isolated nature of Botanisk, it has functioned as a trap for atmospheric deposition, thus making it an ideal site for historical reconstruction of atmospheric deposition.

The primary objective of this study was to utilize a variety of proxies in a sediment core to reconstruct known historical events in Copenhagen, Denmark. These markers could

then be used to further constrain the dating of the core itself beyond the limits of radiochronological methods, thus providing an accurate geological archive going back 400 years. While the use of only one of these markers would not, in and of itself, provide an appropriate confirmation of the geochronology of the core, a suite of chemical analyses can independently cross-validate the accuracy of these dating methods. Additionally, this study provides a better understanding of the ways in which certain historical events, such as fires or changes in fuel sources, have altered the air quality of the region.

4.3 Materials and Methods

4.3.1 Site Information and Sample Collection

Sediment cores were sampled from Lake Botanisk in Copenhagen's Botanical Garden in the winter of 2011. The cores (150 cm long) were collected through the ice and were sub-sectioned every cm depth in the lab after retrieval. Sediment intervals were then freeze-dried and sent to the lab at Texas A&M University at Galveston, where each sediment sub-sample was then homogenized using a ball mill prior to analyses. The sediments were dated by the National History Museum of Denmark and the Geological Survey of Denmark and Greenland using ^{210}Pb and ^{137}Cs dating methods for the last 100-120 years. To constrain the lower portions of the core, synchronization points were identified as visible color changes that appeared in all of the sediment cores taken from the lake. These points were then dated using known historical events and the sedimentation rates were determined between the points.

4.3.2 Chemical Analyses

Organic carbon (OC) concentrations were determined for all sediment samples that were selected for further analysis (approximately every other sample). Sediments were acidified to remove any excess carbonates using a wet chemistry method. Briefly, ~ 0.5g of dried sediment was acidified twice for 30 minutes in 1N HCl. After acidification, sediments were dried thoroughly at 60ºC. OC and total nitrogen (TN) were then determined using a Costech elemental analyzer. Standard reference materials (NIST, SRM 1941b) were also

included with each set of samples to ensure accuracy. The measured %OC and %TN of the SRMs (3.17 and 0.27% respectively) fell within the certified range (2.99 ± 0.24% and <0.5% respectively). The coefficient of variation (CV) for both analyses was 6% and 7% respectively.

The analytical procedure for the quantification of PAHs was followed according to methods outlined by Kuo et al. (2011). Extraction of the PAHs was accomplished by spiking ~1 g of dry and homogenized sediments with PAH surrogate standards (d10-phenanthrene and d12-chrysene) and extracting them with an accelerated solvent extractor (Dionex ASE 200) using dichloromethane as a solvent. Resulting extracts were purified using alumina column chromatography and concentrated in hexane. GC-internal standards (d10-fluorene and d12-benzo[a]pyrene) were added to the final extracts prior to gas chromatography mass spectrometry (GC-MS) analysis. One sample of a standard reference material (NIST, SRM 1944) and a method blank were also included in each run to test for accuracy. Method detection limits for target PAHs averaged 1.0 ± 1.6 ng/g and method blanks tested below the detection limits for each individual PAH. The PAHs from the SRMs fell within the ± 20% variability of the certified values. Separation and quantification of PAHs were performed using gas chromatography–mass spectrometry (GC/MS) with a Varian Ion Trap 3800/4000 system fitted with a fused silica column (VF 5MS, 30 m x 0.25 mm i.d., 0.25 μm film thickness; Varian Inc.). The following compounds were included in the pyrogenic PAHs: pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluroanthene (BbF), benzo[k]fluorathene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IP), dibenz[a,h]anthracene (DA), and benzo[g,h,i]perylene (Bghi).

In addition to this, chemo-thermal graphite black carbon (GBC) analysis (Gélinas et al., 2001; Louchouarn et al., 2007) was employed to identify BC produced at high temperature and containing higher quantities of soot. Acidified samples were treated twice a mixture of 1N hydrochloric acid (HCl) and 10% Hydrofluoric acid (HF) for 12 hours to ensure demineralization. To remove the hydrolysable organic material (HOM), the samples were

then treated with increasing concentrations of trifluoroacetic acid (TFA) that had been purged with argon. The samples were treated for 24 hours with 6N HCl at 100ºC to completely remove any HOM before being rinsed and allowed to dry. After a thermal oxidation treatment (375ºC for 24 hours) to remove all non-soot BC, the samples were then analyzed along with standard reference materials using a Costech CHN elemental analyzer to determine the amount of carbon remaining in the samples. Average variability from replicate samples was 15.3 ± 11.3%.

In addition to PAHs and BC, the Hg content was analyzed for the entire core using a Direct Mercury Analyzer (DMA-80, Milestrone). Samples did not require any pre-treatment and standard reference materials (NRCC, MESS-3, Marine sediment; NIST 2702 Inorganics in Marine Sediment; and NRCC, PACS-2 Marine sediment) were included approximately every 10 samples to ensure that the machine was calibrated properly and reporting accurate measurements. The Hg from the SRM's fell within ± 1.5% of the certified values for the MESS-3, ± 6.4% of the certified values for the NIST 2702, and ± 15.5% of the certified values for PACS-2.

The concentration of lignin oxidation products (LOPs) was also analyzed using the method developed by Hedges & Ertel with modifications according to Louchouarn et al. (2010). Briefly, samples were thermally oxidized with ferrous ammonium sulfate ($(NH_4)_2FE(SO_4)_2 \cdot 6H_2O$), cupric oxide (CuO) and oxygen free sodium hydroxide (NaOH) in a GC oven. The extracts were then spiked with a surrogate standard (250 ng/ µL concentration d-7 cinnamic acid) and acidified. Extracts were then solvent exchanged into ethyl acetate and subsequently dried with a solvent concentrator. The dried oxidation products were then resuspended in pyridine and derivatized before being injected into a GCMS fitted with a Varian Ion trap and a fused silica column for analysis. Duplicates and standard reference materials (NIST 1941b) were included with each set of samples that was analyzed in order to monitor accuracy and account for loss. Sig8 values for SRM's averaged 0.15 ± 0.02 mg g^{-1} and were within ± 15% accepted values; the mean analytical variability of Sig8 values for replicates was <15%.

4.4 Results and Discussion

Several PAH diagnostic ratios, distinguishing between pyrogenic and petrogenic inputs, have been summarized by various groups (Table A-1). The ratio of benzo[a]anthracene to the sum of benzo[a]anthracene and chrysene (BaA/(BaA+Chry)) was described by Yunker et al. (2002) as an indicator of pyrogenic sources if it ranges from 0.3 - 0.6 and petrogenic sources when < 0.2. Ratios of BaA/(BaA+Chry) throughout the core fall consistently within the pyrogenic source ratio (Fig A-1). In addition, the methylphenanthrenes to phenanthrene ratio (MePhe/Phe) differentiates combustion-derived PAHs (0.4 - 0.7) from petrogenic sources (> 5) (Fig A-1; Elmquist et al., 2007). The low values for this ratio in the Botanisk core (0.8 ± 0.5) confirm combustion as the predominant source of PAHs to this sedimentary environment, with the exception of a slight shift towards petrogenic signatures (1.5 ± 0.2) in the early 1600's to approximately 1780. This may be due in part to diagenetic PAHs accumulating on particulate matter or to a small fraction of alkylated PAHs derived from petrogenic sources (e.g. tar) during that period. Furthermore, the ratio of Fluoranthene to the sum of Fluoranthene and Pyrene (Flu/(Flu+Pyr)) holds fairly constant at approximately 0.59 ± 0.02 throughout the depth of the core (Fig A-2). A diagnostic ratio of this value indicates that PAH concentrations in the core are dominated primarily by combustion of coal and/or wood (Torre-Roche et al., 2009). The combination of these ratios thus provides independent confirmation that combustion processes are responsible for the majority of PAH inputs to these sediments over the last 400 years of history (Figs A-1 and A-2). Specific ratios (see discussion below) suggest that shifts in fuels, combustion activities, and technology have led to different levels of input to the system.

4.4.1 1600 - 1860: Wood and War

Two diagnostic ratios were used for the discrimination of softwood combustion inputs from other pyrogenic sources throughout the Botanisk core. Retene is selectively enriched in the smoke from wood combustion (Ramdahl, 1983), and as such Yan et al proposed (2005) that the ratio of retene to the sum of retene and chrysene (Ret/(Ret+Chry)) is indicative of wood combustion if it has a value of ranging from 0.9 - 1.0. This is contrasted to ratios ranging from 0.17 - 0.45, which indicate oil or coal combustion. Similarly the ratio of 1,7-dimethylphenanthrene to the sum of 1,7-dimethylphenanthrene and 2,6-dimethylphenanthrene (1,7-DMP/(1,7-DMP+2,6-DMP)) was described by Yunker et al. (2002) as a means to delineate PAHs derived from wood combustion (ranging ~0.8 - 1.0) from those that are produced from coal/lignite combustion (ranging ~0.45 - 0.7), and vehicular emissions (< 0.45; Table A-1). The combination of these ratios shows that from 1600 to the middle of the 19th century, Copenhagen was largely dominated by softwood combustion (Fig 7). The ratio of 1,7-DMP/(1,7-DMP+2,6-DMP) is within the range 0.7-1.0 throughout the bottom half of the core and remains there until approximately 1860, when it rapidly drops towards the range of coal combustion. This is paralleled quite closely by the Ret/(Ret+Chry) ratio despite its greater variability. The marked decrease in this latter ratio around the end of the 19th Century is synchronous with a significant increase in PAH concentrations (Fig 7) and points to a shift in combustion inputs during this period.

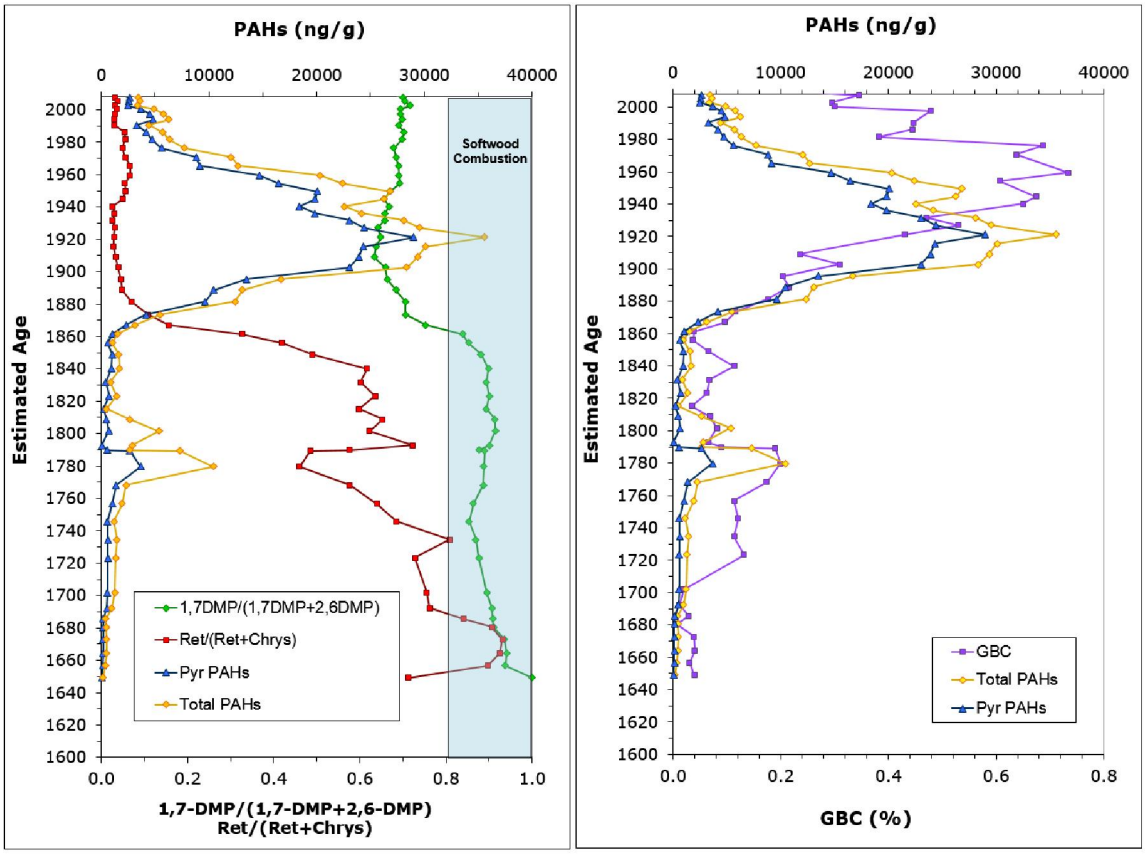

Figure 7. Comparison of softwood diagnostic ratios 1,7-DMP/(1,7-DMP+2,6-DMP) to Ret/(Ret+Chrys).

From 1650 to the mid 1750's, the average total PAH and pyrogenic PAH concentrations remain close to background (~660 and ~280 ng/g, respectively). Similarly, BC concentrations hover at background levels (~0.04%) from 1650 to 1700. Although BC can be produced via wood combustion, temperatures need to be high enough (Meyer, 2012; Schmidt and Noack, 2000). The constant 1,7-DMP/(1,7-DMP+2,6-DMP) during the early period of the core are likely due to the use of closed wood stoves, kilns, or forges. Two peaks in BC and PAH concentrations occur during the 1760-1820 period. The largest of these peaks (~1780 - 1790: 10400 and 3700 ng/g for total and pyrogenic PAHs, respectively) corresponds to a decrease in the Ret/(Ret+Chry) ratio (Fig 7). It is possible that this marked change in both concentrations and signatures was largely due to a fire that occurred in Copenhagen in the year 1795 when warehouses used for the storage of coal

and wood barrels caught fire at the navy's old base in Gammelholmn. The fire spread and consumed 941 houses, destroying much of the medieval portion of the city (Jessen, 1898). In light of these events, the combustion of the navy's coal stores is a probable source for the observed increase in pyrogenic PAHs and the resulting decrease in the diagnostic ratio in the core at that particular depth. Additionally, the percentage of BC simultaneously peaks at 0.19%, which is consistent with large-scale emissions of coal-derived combustion.

The second peak in total PAH concentrations occurs at approximately 1805. This peak coincides with the Napoleonic Wars, during which Denmark experienced two major battles. The first of these battles was in 1801 and primarily involved the British destruction of several Danish ships. The second battle occurred in 1807 and involved a three day long bombardment of the city which destroyed approximately 30% of its buildings. The total PAH concentrations (~5400 ng/g) for this period are approximately half those of the 1780 peak. Interestingly, the pyrogenic PAHs (680 ng/g) only increase to approximately a quarter of those observed in the preceding years. Although there is a corresponding peak in BC at this time, like the PAH peak it corresponds to only half (0.08%) of the previous BC peak. It is possible that this is due, in part, to a lack of coal combustion that was seen in the 1795 fire or to higher inputs of petrogenic residue PAHs (lower molecular weights and higher alkyl content; Wang et al., 1999) resulting from the bombardment of the city. The slight increase in the MePhe/Phe ratio during that time (Fig A-1) supports the latter hypothesis.

Lignin and Hg concentrations in the lower core undergo also changes that parallel historical construction on and alterations to the moat from the years 1650-1850. The moat surrounding the city of Copenhagen was not constructed until the year 1650; until this time the Rosenborg castle had existed outside the city and relied on a supply of water that came from a trench connecting Lake Sortedam to the castle's wash houses and fountains. When the moat was constructed, it bisected the trench between Rosenborg castle and Lake

Sortedam near the current site of Lake Botanisk. From this point on, the trench was used to provide the moat with a source of fresh water.

In the late 1600's to early 1700's the concentrations of both lignin and Hg rapidly increase tenfold (from <1.0 mg/g to 7.0 mg/g and approximately 120 to 1,270 ng/g, respectively) and remain elevated until the late 1700's. This increase is likely related to the direct inputs of water and sediments from Lake Sortedam which drained a larger watershed than Botanisk. Inputs of terrigenous organic matter from Lake Sortedam may have acted as a carrier phase of Hg and thus a source of this metal to the small receiving water body (Fig 8). The strong correlation between lignin and Hg (R^2= 0.82; Fig A-4) between 1650 and 1870 further supports this interpretation. It is interesting to note that the water quality of both Lake Sortedam and the moat were so poor in the early 1700's that the city made several attempts to improve water quality, although this was done without much success. In the 1800 an architect named General Ernest Peymann undertook a project that renovated the trench in stages and covered several large portions. Peymann also eventually replaced the trench with a pipe that emptied directly into the region of the moat that would later become Lake Botanisk. During these renovations the line had to be flushed several times which likely accounts for the variations in lignin and Hg concentrations from 1790 to approximately 1874. The moat was filled in 1874 leaving Botanisk as an isolated body of water and acting more like an atmospheric trap than a drainage basin.

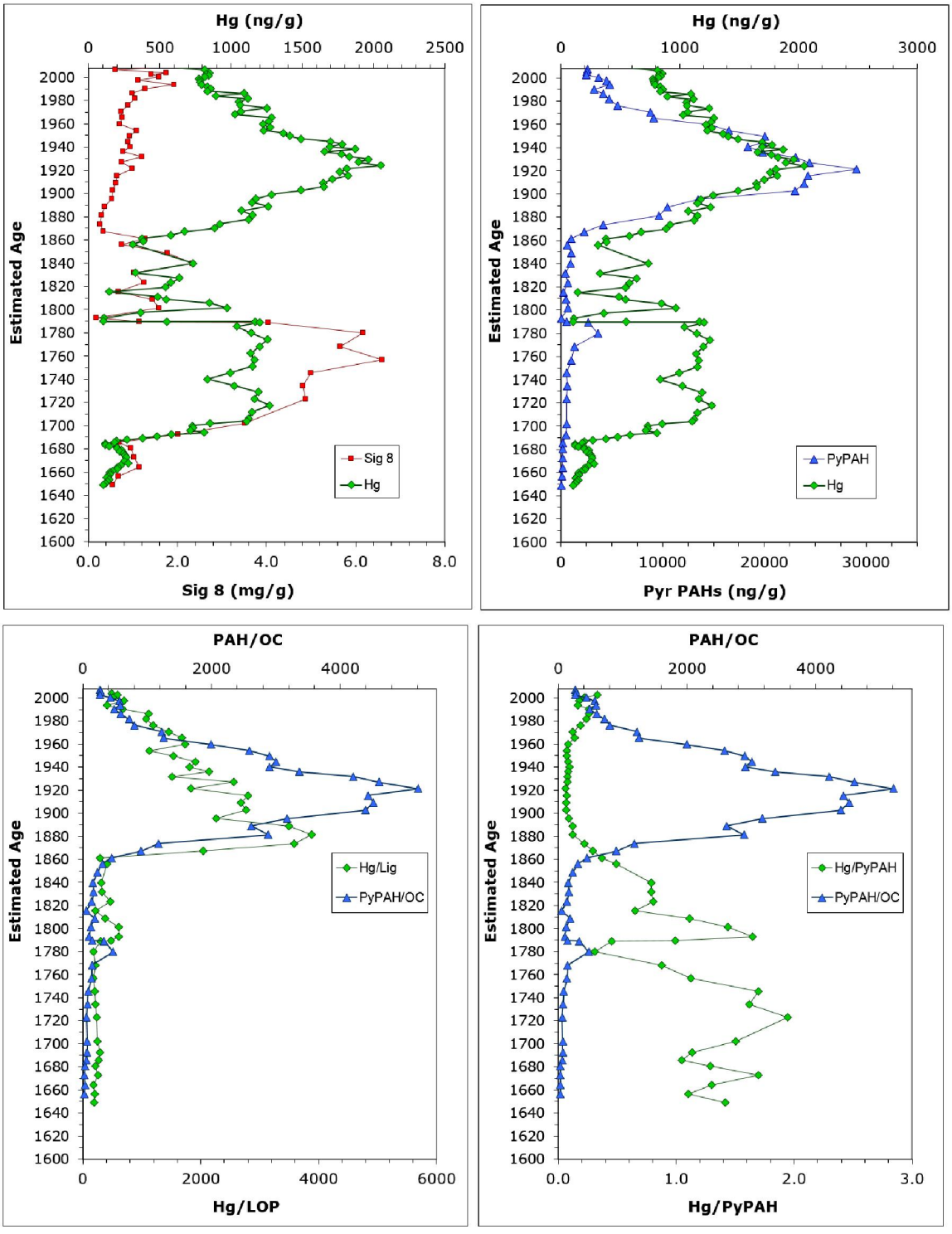

Figure 8. Concentrations of Hg versus lignin (top left) and Hg versus PyPAHs (top right). The bottom graphs depict Hg normalized to lignin (left) and PyPAHs (right). When normalized to lignin, Hg drops down to background levels in the lower half of the core. Similarly, when normalized to PyPAHs, Hg drops to background levels in the upper half of the core

4.4.2 1860 - Mid 1900's: Industrial Revolution and the World Wars

In the mid 1800's, Denmark experienced the onset of its Industrial Revolution, during which the import of coal increased markedly (Fig 9) and wood burning became less common. This is evidenced by the rapid increase in PAH concentrations starting in ~1860. Simultaneously, the ratios of both Ret/(Ret+Chry) and 1,7-DMP/(1,7-DMP+2,6-DMP) drop significantly from their characteristically high pre-Industrial levels (Fig 7). By 1890, Ret/(Ret+Chry) fell to a ratio of approximately 0.05, demonstrating a marked decrease in the proportional use of wood as a major fuel source. Simultaneously, the ratio of 1,7-DMP/(1,7-DMP+2,6-DMP) drops to approximately 0.5 - 0.65, within the diagnostic range of coal and lignite combustion. From the 1860s, the total PAH and pyrogenic PAH concentrations continue to increase steadily till they reach a peak (35,600 and 29,100 ng/g for total and pyrogenic PAHs, respectively) at approximately 1920. These values are two orders of magnitude higher than background values measures in pre-1700 sediments. The increase of pyrogenic PAHs corresponds with importation and consumption of coal throughout this time (Fig 9). Due to the relatively inefficient (i.e. lower temperature) coal combustion methods during the early part of the 20th century, pyrogenic PAH emissions were high with large particulate matter (PM) emissions per ton of coal consumed (Louchouarn et al., 2007).

The BC concentrations also begin to increase in the 1860's, however they do so at a slower pace than the PyrPAHs and peak approximately in 1960, with a 40 year delay after the PAH peak. A peak in coal consumption is suggested right after both the first and second world wars (1914 - 1918 and 1939 - 1945, respectively), as recorded by sudden increases in PAH concentrations following dips or slow rates of increase. Following WWI, Denmark began to shift its fuel sources to incorporate a higher proportion of petroleum. The import of oil began in ~1920 and continued to increase until WWII, when nearly all importation ceased (Fig 9) till after the war. It is interesting to note that the BC profile does not follow this trend, even during reduced coal importation during the wars. It is possible that this is due to the fact that coal was still being combusted (although at lower rates than

previously), most likely in plants that would have high combustion efficiency and produce larger amounts of soot BC as opposed to PAHs.

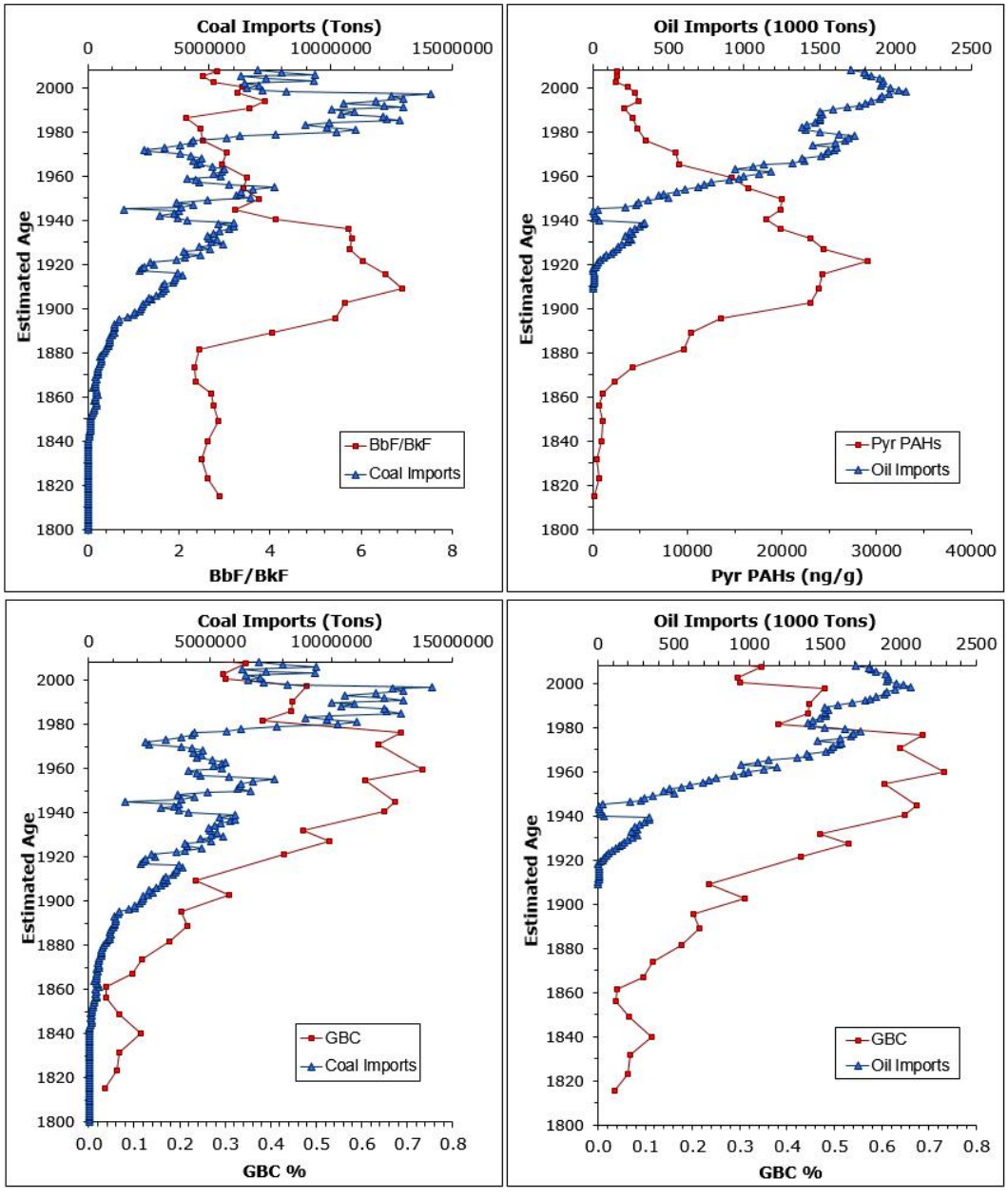

Figure 9. Importation of coal into Denmark with BbF/BkF (Top left) and GBC (Bottom left). Oil importation in Denmark with pyrogenic PAHs (Top right) and GBC (Bottom right).

Between 1860 and the mid-1900's Hg concentrations peak around the mid-1920 (~2,050.0 ng/g) and then slowly taper off. In 1871-1874, the moat around present-day Lake Botanisk was completely filled in, leaving it and a few other lakes to the north of the city as isolated bodies of water. It is during this time that Hg trends become decoupled from lignin, likely due to the significant reduction in terrigenous organic matter entering the lake (Peymann's line was still functional and connected to the lake but was not heavily used). Furthermore, construction and work on the lake after this point were minimal and lignin concentrations remain low; the Hg peak is therefore unlikely to be due to perturbations in sediment or external water inputs. Rather, Hg concentrations become strongly correlated with the PyrPAH trend (R^2=0.86, Fig A-5), indicating that Hg input to the lake post 1870s, is predominantly due to atmospheric deposition from combustion processes during these years.

4.4.3 1950's - Present: Post War Technology, the EPA, and the New Millennium

Following 1945, importation of petroleum resumed and increased while that of coal, after a small resurgence post WWII, started to decline (Fig 9). The rapidly declining PAH concentrations during these two decades show the influence of shifts in fuel consumption from coal to oil as well the advancements in combustion technology which enabled more efficient burning of both fuel sources. These advancements combined with the increase in fuel importation explain why the BC trend continues to increase during these years, reaching a peak around 1960 at ~0.73% (Fig 7). These trends continued until the early 1970's when a total oil embargo was placed on Denmark as a result of its aid to the USA and Israel during the OPEC oil crisis. Because of this embargo, Denmark's petroleum imports were significantly reduced and it was forced to increase its importation and utilization of coal once more (Fig 9).

The shift in fuel sources as a result of the embargo is reflected in a small increase in PAH concentrations and a more noticeable resurgence in BC concentrations. A significant increase in the ratio of Benzo[b]fluoranthene (BbF) to Benzo[k]fluoranthene (BkF) is also evident (Fig 9). This ratio is particularly useful for the characterization of PAH emissions

from coal combustion (Louchouarn et al., 2012). In the Botanisk core, the BbF/BkF ratio shows a strong relationship (R^2=0.74) with pyrogenic PAH concentrations since the onset of the Industrial Revolution in the 1860's (Fig A-3). It is important to note that while this ratio increases in tandem with the peak in coal imports during the 1980 - 1990's, the total and pyrogenic PAH levels remain significantly lower and experience much less of an increase. Likewise, the increase in BC, while larger than that observed in the PAHs, is still approximately one third smaller than that observed during the 1960's. These shifts are most likely due to the Environmental Protection Act in 1974 which enabled Denmark to begin enforcing air quality regulations. Following this act, further legislation was put in place imposing limits on the levels of pollutants and PM that could be emitted from a broadening sector of industries and combustion plants. High levels of coal importation continued from 1980 - 1997 until the oil embargo was lifted and petroleum importation into Denmark could recover. However, the oil crisis of 1973 had caused Denmark to reevaluate its fuel utilization policies and make a push towards more renewable energy (Fenger, 2003).

In the mid to late 1980's, Denmark began to move towards achieving a more stable economy based upon mixed fuel sources and lowered emissions. A shift to less energy consuming activities was underway and wind was adopted to a greater extent as a renewable energy source (Walsh/Samso, 2009). In addition, natural gas became a significant contributor to the gross energy consumption of the nation (SI Fig 11). These changes resulted in decreases in the total and pyrogenic PAH emissions in Copenhagen as well the in ratio of BbF/BkF, which drops down below preindustrial levels by the early 2000's (Fig 9). It is interesting to note that while a decrease in PM has been observed due to cleaner forms of combustion, a recent study (Fenger 2003) found that emissions of BaP, BbF, BkF, and indeno(1,2,3-cd)pyrene (IP), have actually increased from 1990 - 2000 (Fig A-4). These increases are credited primarily to nonindustrial emissions, such as domestic fireplaces. When compared to the results of this study, it is seen that the ratio of BbF/BkF does indeed show a slight increase in the upper core (Fig A-3). However, this increase is seen slightly after the year 2000, a discrepancy which could be credited to the slight

mixing of sediments in the lake. The ratio of 1,7-DMP/(1,7-DMP+2,6-DMP) provides the strongest support of the recent use of domestic wood burning, as it is seen to move slightly back into the softwood combustion range of >0.7 (Fig 7). BC levels are also observed to increase in the topmost layer of the core. It is possible that this is due to vehicle fleet emissions from diesel combustion (Jiang et al., 2005; Lima et al., 2005). Despite the recent decreases in overall emissions in Copenhagen, PAH and BC concentrations are still tenfold higher than preindustrial levels.

Lake Botanisk provides a unique opportunity for monitoring BC and PAH trends over time due to its relative proximity to a major urban city and its long undisturbed record (~400 years). Furthermore, its isolation from other bodies of water since the onset of the Industrial Revolution suggests that PyC concentrations within the sediments accumulated in the last 150 years are predominantly derived from atmospheric deposition within the lakes watershed. Very few urban lakes exist with such an extensive history and which allow for a detailed reconstruction of past combustion trends resulting from the urban and industrial development of a single city. A similar study was conducted in Aspvreten, Sweden, just northeast of Lake Botanisk; BC and PAH peaks in sediment cores from the Stora Frillingen Lake were more strongly correlated to each other and did not occur until the mid to late 1900's despite having an Industrial Revolution around the same time as Copenhagen (Elmquist et al., 2007). It is possible that the lag observed in the Aspvreten core is due to the more remote setting of the sample site. Such regional differences highlight the impacts that local history can have on atmospheric deposition records and therefore calls into question the feasibility of constructing large scale models that accurately predict emissions of PyC based upon fuel consumption data at the national level (Novakov et al., 2003).

5. SUPPORTING INFORMATION

5.1 Historical Information

Copenhagen, the capital of Denmark, was founded in the mid-12th century and has experienced significant growth and urbanization since its birth. Under the rule of Christian IV, the city became a stronghold in the 17th century as large embankments were built surrounding the city. Today Copenhagen is the major cultural, financial, and governmental center of Denmark. Its rich chronicled history makes this city an ideal site for historical reconstruction studies. The following timeline chronicles not only the physical changes that have shaped what is now Lake Botanisk, but also includes major events that were likely to have impacted the air and water quality of both the city's watershed and it's moat.

1618 – A trench was built between Rosenborg castle and Sortedam Lake to provide the castles wash houses and fountains with water.

1650 – The moat was constructed around the city of Copenhagen, intercepting the trench that ran to the castle. The trench now supplied the moat with fresh water from Sortedam; the inlet for the trench was close to the present location of Lake Botanisk.

1700 – Around this time, several attempts were made to clean the water in both the moat as well as Lake Sortedam.

1706 – Rosenborg ravelin built. A ravelin is a triangular fortification that is built on the outside of a fortress and is typically surrounded by a moat.

1728 – Largest fire in the history of Copenhagen. Destroyed nearly one third of the city directly to the west of present Lake Botanisk.

1790 to early 1800's – Construction began on Peymann's line. The initial line was covered and contained a series of locks. Flushing of the line was common during this period and likely resulted in inputs of terrigenous organic matter to the moat.

1795 – Second fire of Copenhagen. Started at the Navy's base in Gammelholm when the coal warehouse caught fire. Over 900 houses were destroyed or damaged.

1801 – Napoleonic Wars, First Battle of Copenhagen. The British destroyed much of the Danish fleet of ships in battle.

1807 – Napoleonic Wars, Second Battle of Copenhagen. British bombarded the city and destroyed many buildings, the Danish fleet was also surrendered by General Peymann at this time.

1853 – A refugee camp for citizens of Copenhagen who were fleeing a cholera epidemic was established right outside the moat. It was this outbreak that prompted the expansion of the city beyond the moat. Records indicate that wastewater was discharged into the lake for a short period of time.

1860 – Denmark begins its Industrial Revolution

1871 to 1874 – Several portions of the northern moat were filled in, leaving Botanisk as an isolated lake. Peymann's line still supplied fresh water to the lake.

1914 to 1918 – World War One

1939 to 1945 – World War Two

1941 – Peymann's line was completely closed off and no longer allowed the flow of water between Lake Sortedam and Lake Botanisk.

1973 – OPEC Oil Embargo

1974 – Danish Environmental Protection Act and Clean Air Initiatives

Georeferenced maps of Copenhagen throughout its history are useful for visualizing the changes that have taken place in the city throughout its development and expansion. Between the years 1728 and 1853 the developed area of Copenhagen experienced a 13% increase from ~12 km^2 to ~14 km^2, a growth rate of only 0.01 km^2 $year^{-1}$ (Fig 10). Nearly all of the growth during these years took place within the city walls. The population of the city increased from about 75,000 to 129,700 during these years until the 1850's when a cholera epidemic broke out due the large population density. It was this epidemic that caused the city to begin filling in the moat and expanding outside of the original city walls. From 1853 to 1900 the city grew outside the bounds of the moat and experienced an increase of more than 75%, expanding to an area greater than 59 km^2 at a growth rate of more than 1 km^2 $year^{-1}$ (Fig 10). During these 50 years the population increased from 129,700 to more than 400,500 (provided by the Copenhagen Municipality, Administrative Division). The increased production (agricultural as well as industrial) and energy capabilities that arose as a result of the Industrial Revolution in the mid 1800's as well as the substantial increase in coal importation were arguably important factors in shaping the development of the city of Copenhagen.

In this study, the processes of urbanization and industrialization in Copenhagen have been attributed as the driving force behind the increase in emissions and combustion byproducts. As such these processes are viewed as being linked to each other, with advancements in industrialism and industrial technology facilitating the growth in urbanization. In some cases however, industrialism is not the driving factor behind urbanization; rather agricultural developments and productivity functions as the main push behind urban development. Denmark is somewhat unique in that despite being a fossil fuel poor country, its urbanization stemmed largely from an agricultural revolution due to technological developments in farming equipment; these advancements were responsible for a portion of the coal consumption in the country due to the use of steam power. In particular this allowed the country to develop booming dairy/creamery and slaughterhouse industries which bolstered the nation's economy (Henriques and Sharp, 2014; Hyldtoft, 2012).

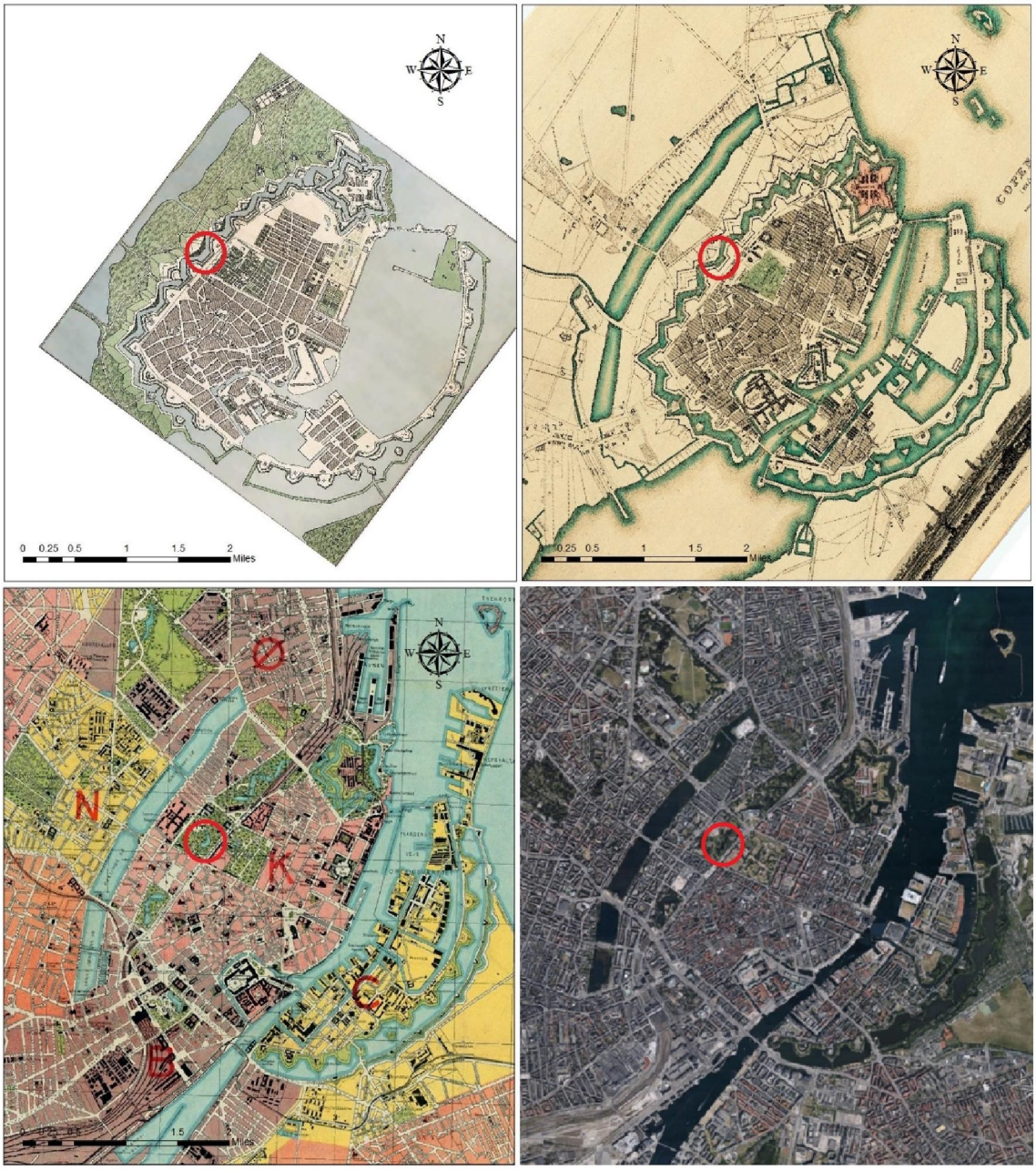

Figure 10. Maps of Copenhagen since the 18th century with the location of Lake Botanisk circled in red. Between the years 1728 (top left) (Arnøldt, 1728) and 1853 (top right) (Clarke, 1853) the developed area of Copenhagen experienced a 13% increase from ~12 km^2 to ~14 km^2. From 1853 to 1900 (bottom left) (Politikens forlag, 1900) the city grew outside the bound of the moat and experienced an increase of more than 75%, expanding to an area greater than 59 km^2. The city at the present (2015) is located at the bottom right (Google Earth, 2014).

The urbanization of Denmark is arguably due to combination of economic and technological advancements. Despite having no domestic coal deposits, the availability of international coal to the nation was a driving factor in allowing these advancements to take place. In contrast to other European countries at the time, coal was imported to Denmark for relatively low costs, thus allowing coal to surpass wood and peat as the major energy sources as early as 1854 (Henriques and Sharp, 2014). Not only did this allow for expansion of the nation's creamery industry, but it also provided major cities like Copenhagen with substantial resources to support economic developments and urban infrastructure like coal-fired gasworks, railroads, lighting, etc. As such, both the industrialization as well as the urbanization of Copenhagen following 1860 can be said to be fairly dependent upon the importation of coal (and eventually oil) and the advancements of combustion technology (Anderson, 2015).

5.2 Denmark's Energy Sector in Recent Years

Denmark has moved towards more renewable energy since WWI when the shortage of fossil fuels pushed them towards adopting wind energy for rural power stations (Currie et al., 2002). While the country sill utilizes coal and oil, they have moved towards incorporating natural gas and several forms of renewable energy in an effort to minimize carbon emissions (Fig 11). In fact, Denmark is ranked as one of the least energy intensive of high-income countries due to its technological advancements, infrastructure, energy-efficiency programs, etc. (Schipper et al., 1992). The significant reduction in PAH emissions since the enforcement of environmental air standards is likely a result of these efforts. It is important to note that despite a commendable push towards greener fuel usage and energy efficiency, PAH and BC levels in recent sediments of Lake Botanisk are still much higher than background levels. Further reductions in these emission levels may help to reduce these contaminants, however the large population size and ongoing need for energy may confound these efforts.

In particular the increased use of mobile vehicles and other forms of transportation (air, railway, sea, etc) within Copenhagen is likely a major factor contributing to the continuing

elevation in BC concentrations. The transportation sector alone accounted for approximately one quarter of the final energy expenditure of Denmark in 2012, an increase from the previous 30 years (Fig 12). The 2009 Copenhagen Traffic Report estimated that there was about a 20% increase in the car traffic of Copenhagen between the years 1990 and 2009 (Torslov, 2010). It was estimated that during these years the number of private car owners increased by approximately 50%. Despite the fact that the city is pushing towards increased use of public transportation and cycling, the sheer increase in population numbers within the city has continued to drive up the number of motor vehicles in use in the city. Additionally many European countries, including Denmark, have experienced an increase in the use of diesel fueled motor vehicles (Fig 12; Danish Energy Agency, 2014). Diesel fuels consumed by heavy duty trucks were found to produce more LMW PAHs and BC than their lighter weight and gasoline consuming counterparts (Miguel et al., 1998). As such, the transportation sector likely plays an important role in contributing the elevated levels of PAHs and BC observed in the Botanisk core.

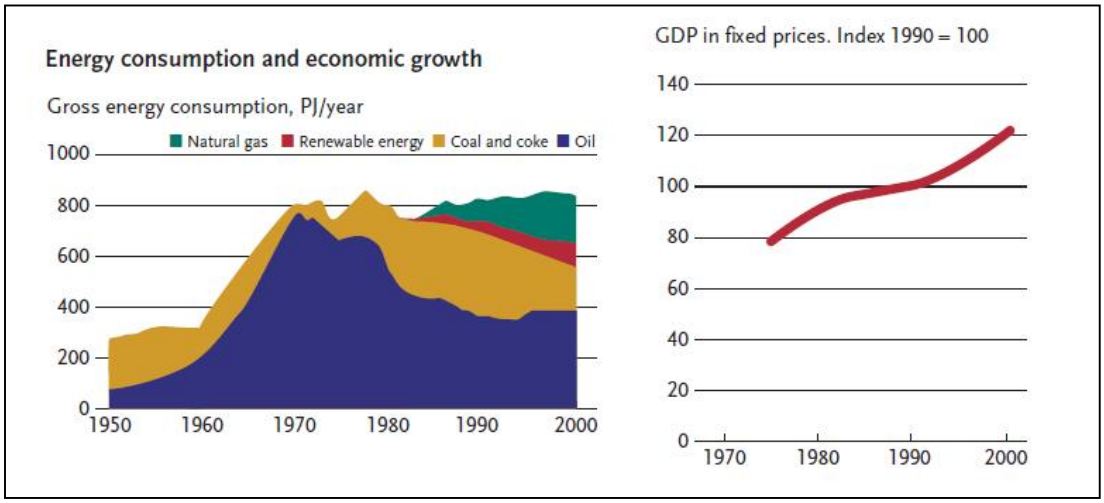

Figure 11. Denmark's energy consumption since 1950. Gross energy consumption according to fuel sources (left) as well as the increase in GDP as a result of lowered energy usage (right) (Fenger, 2003).

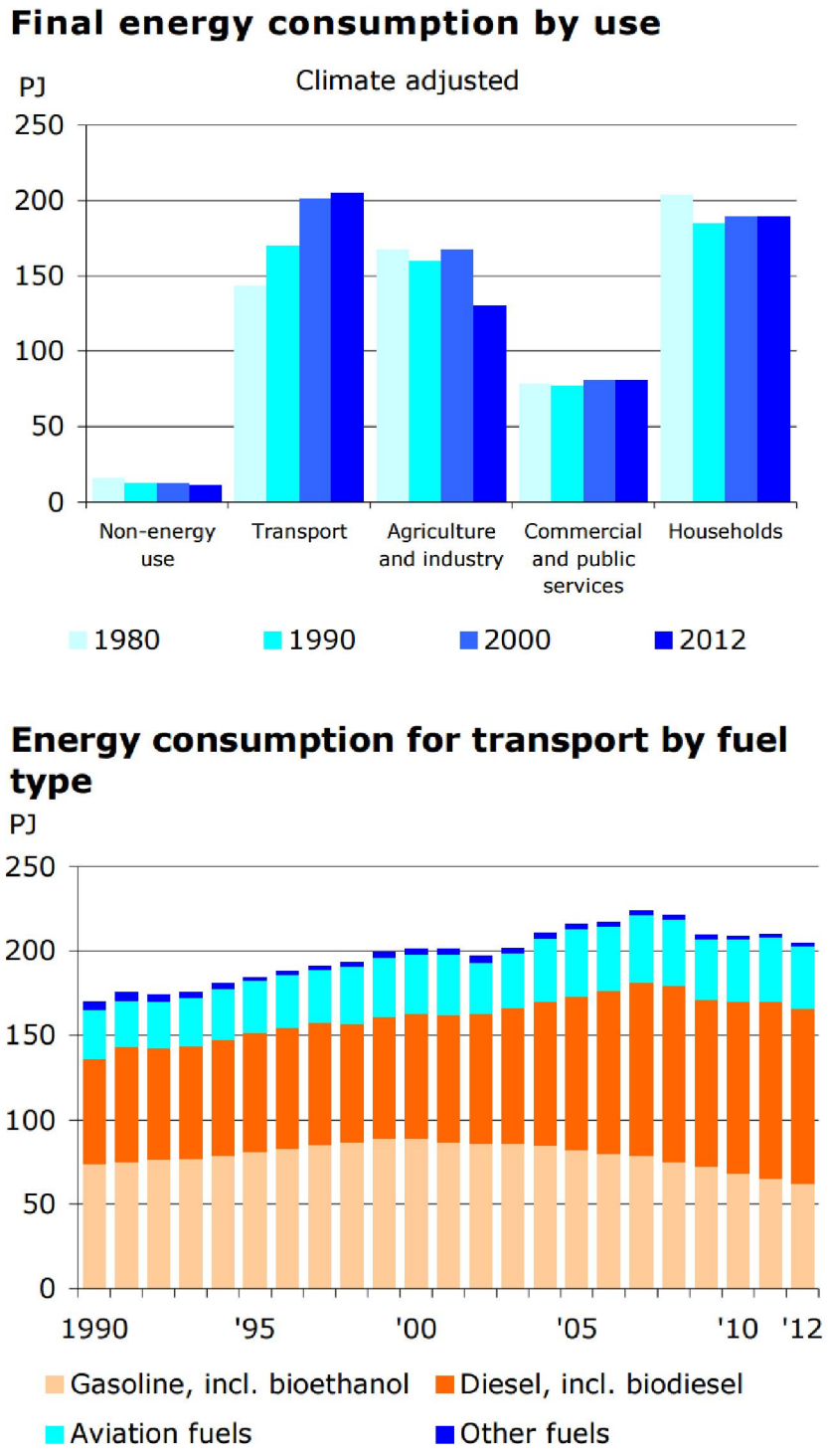

Figure 12. Breakdown of Denmark's fuel use in recent years. Climate adjusted energy consumption in Denmark according to sector between the years 1980 and 2012 (top). Energy consumption for the transportation sector in Denmark by fuel type between the years 1990 and 2012 (bottom) (The Danish Energy Agency, 2014).

6. CONCLUSIONS

This study demonstrates the usefulness of multiple chemical tracers in the reconstruction of historical combustion records. Due to its isolation from other bodies of water, its relative proximity to a major urban city, and its long undisturbed record (~400 years) Lake Botanisk provides a unique opportunity for monitoring atmospheric deposition trends within the lake's watershed over time. Very few urban lakes exist with such an extensive history which allows for a detailed reconstruction of past combustion trends resulting from the urban and industrial development of a single city. Time-trend analyses of combustion-related contaminants in sediments from such lakes allows for an evaluation of changes in air and water quality with respect to growing populations in urban centers. Such trends can also illustrate the efficacy of past emission regulations and policies (Brandenberger et al., 2008; Elmquist et al., 2007). Furthermore, the results of this study provide a background against which current levels of anthropogenic combustion byproducts can be compared, thus making it possible to determine whether emissions have returned to preindustrial levels.

Combustion trends as delineated by PAH source diagnostic ratios parallel fuel shifts and technological advancements throughout Denmark's history. From 1600 - 1850 wood was the primary fuel source, resulting in the production of high levels of alkylated PAHs (Fig 13). During the Industrial Revolution, Denmark shifted from the use of wood towards coal. The relatively inefficient combustion methods of from 1860 to ~1950 led to high levels of PM and larger ratios of low molecular weight (LMW) to high molecular weight (HMW) PAHs. Following WWII, Denmark again shifted its fuel source to favor the use of petroleum. However due to advancements in combustion technology, lower levels of HMW PAHs are produced during this time. The OPEC oil crisis forced the nation to revert back to the use of coal in 1973. Very low PAH emissions are seen at this time due to the enforcement of air quality acts as well as the improved efficiency of combustion and emission abatement approaches. Finally, from ~1980 on, Denmark has moved towards the use of a combination of petroleum, coal, and natural gas. All of these fuels sources are

currently producing very low emissions due to the large advances in emission control technologies. Because the results of this study can be compared to a known historical record they may be used to support the accuracy of certain source diagnostic ratios to determine the source of PAHs in sediment cores.

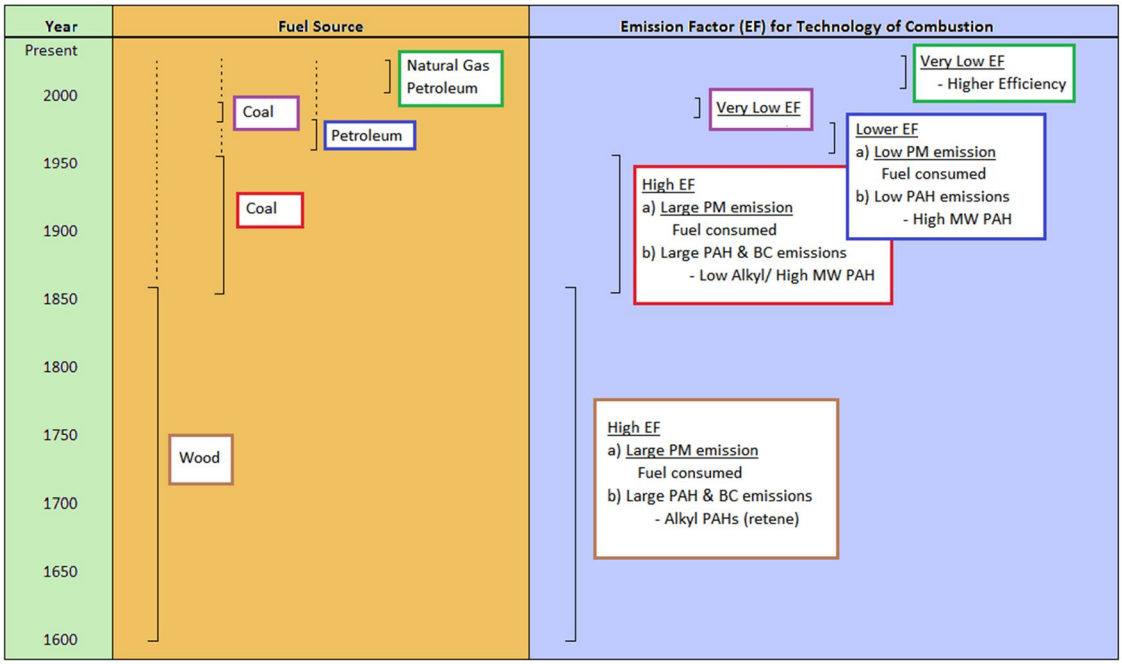

Figure 13. Progression of fuel sources utilized in Denmark through time with corresponding emission factors and PAH characteristics.

It is important to note the significant impact that regional history has on the atmospheric deposition record. A similar study conducted northeast of Lake Botanisk, in Aspvreten, Sweden, yielded BC and PAH peaks that were more strongly correlated to each other and did not occur until the mid to late 1900's despite having an Industrial Revolution around the same time as Copenhagen (Elmquist et al., 2007). If a sediment core is taken within the watershed of an urban area, it will likely show a marked increase in PAHS, BC, and perhaps some heavy metals around the time that that region experienced its Industrial Revolution. It is possible that the lag observed in the Aspvreten core is due to the more

remote setting of the sample site. Such regional differences call into question the feasibility of constructing large scale models that accurately predict emissions of PyC based upon data of fuel consumption at the national scale.

One of the limitations of this study is that it is not possible to differentiate between the combustion byproducts that were emitted into the local atmosphere and those that were deposited via long range atmospheric transport. As such the total levels of BC, PAHs, and Hg within the core may be indicative of both local and long range sources. However, the presence of long range atmospheric transport products does not negate local sources as being the driving force behind the trends seen in the Botanisk core. The primary reason for this is that long range transport simply does not supply enough combustion byproducts to overwhelm and alter local trends, particularly in such a large urban area as Copenhagen. Similar studies conducted in regions with little to no local inputs of combustion byproducts (Aspvreten, Sweden) demonstrate significantly lower concentrations of BC and PAHs. To further verify this, a similar study could be conducted in the arctic regions near Denmark to gain a better understanding of the concentrations of combustion byproducts that may have been introduced to Botanisk via long range transport. Additionally, investigating the trends of combustion byproducts in more remote sites in Denmark could elucidate the regional differences due to urbanization or industrialization. For instance, mercury measured in ombotrophic bogs from more isolated regions of northern and southern Denmark (Store Vidmose and Draved Kongsmose, respectively) did not reach concentrations of more than ~400 ng g^{-1} in Draved Kongsmose and ~750 ng g^{-1} in Store Vidmose (Madsen, 1981). This stands in stark contrast to the mercury concentrations of more than 2,000 ng g^{-1} that were detected in sediments from Botanisk. Furthermore, the trends of Hg deposition observed in the bogs were independent from that of the Botanisk core. This difference depositional trends as well as Hg concentrations between Copenhagen and the ombotrophic bogs highlight the impact that local industrial processes (such as the combustion of coal) in Copenhagen had on the air quality of the region in contrast to the long range transport of Hg that is observed in the more isolated regions surrounding Store Vidmose and Draved Kongsmose.

Finally, there is also a need for further clarification of the terms that are used to refer to the PyC continuum. There are a large number of chemical species formed within the PyC continuum depending upon the fuel source and combustion temperature. Such complexity makes it necessary to utilize a variety of detection methods in order to accurately determine concentrations of the various constituents (Hammes et al., 2007; Masiello, 2004). Many studies simply refer to the entire continuum as BC and fail to clarify whether they are discussing chars, charcoals, soot-BC, PAHs, etc. Each of these constituents is unique and therefore their behavior and longevity within the environment differ. Furthermore, the health effects vary greatly between soot-BC and PAHs as they take different pathways once in the human body (Gardiner and Tongeren, 2001; Koelmans et al., 2006). This ambiguity makes it extremely difficult to accurately assign sources to measured emissions and can therefore greatly impact the efficacy of policy making. For instance, policies that place restrictions upon combustion processes that are believed to result in incomplete combustion of organic matter (i.e. those that operate at lower temperatures) may completely disregard the emissions of soot-BC that are produced from high-temperature combustion processes. For the scientific field, such ambiguity makes it difficult to properly interpret previous research and apply it to studies that attempt to clarify the differences within the PyC continuum.

The value of using multiple chemical tracers in conjunction with radiochronological dating methods when analyzing sediment cores is made evident by the results of this study. The concentrations of BC, PAHs, Hg and lignin throughout the core created trends that paralleled known historical events of the region and therefore aided in the reconstruction of an accurate chronology. In sites like Botanisk that have well-recorded historical events, such as fires or wars, these events can be used to explain trends in combustion related contaminants found in sediments. Depositional trends that correspond with these events can then be used to corroborate the accuracy of the dating methods employed. Additionally, a suite of such chemical analyses can aid in understanding how changes in fuel and land use over time has impacted the ecosystem. Ideal sediment cores, such as that obtained from Botanisk, can reveal a significant amount of information about the impacts

of urbanization on a system. Further work should include identifying other lakes in urban regions and employing similar methods to elucidate their unique regional combustion and industrialization history. The results can then be compared to each other to create a body of literature that details the historical impacts of industrialization and combustion processes. Such a database would likely prove extremely useful in the forecasting of possible ecological impacts of future combustion technologies.

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APPENDIX

Table A-1. Diagnostic ratios of PAHs and reported values for various processes.

Ratio	Value Range	Source	Reference
∑LMW / ∑HMW	< 1	Pyrogenic	Zhang et al., 2008
	> 1	Petrogenic	
BaA / (BaA+Chry)	0.3 - 0.6	Pyrogenic	Yunker et al., 2002
	0.0 - 0.2	Petrogenic	
MePhe / Phen	0.0 - 1.0	Pyrogenic	Elmquist et al., 2007
	5.0 - 6.0	Petrogenic	
BbF / BkF		Coal combustion	Louchouarn et al., (2012)
Flu / (Flu+Pyr)	< 0.4	Petrogenic	De La Torre-Roche et al., 2009
	0.4 - 0.5	Oil Combustion	
	> 0.5	Coal and Wood combustion	
Ret / (Ret+Chry)	~ 1	Wood Burning	Yan et al., 2005
1,7-DMP / (1,7-DMP / 2,6-DMP)	0.7 - 0.9	Wood Burning	Yunker et al., 2002
	~0.45 - 0.7	Coal/ Lignite	
	<0.45	Vehicle Emissions	

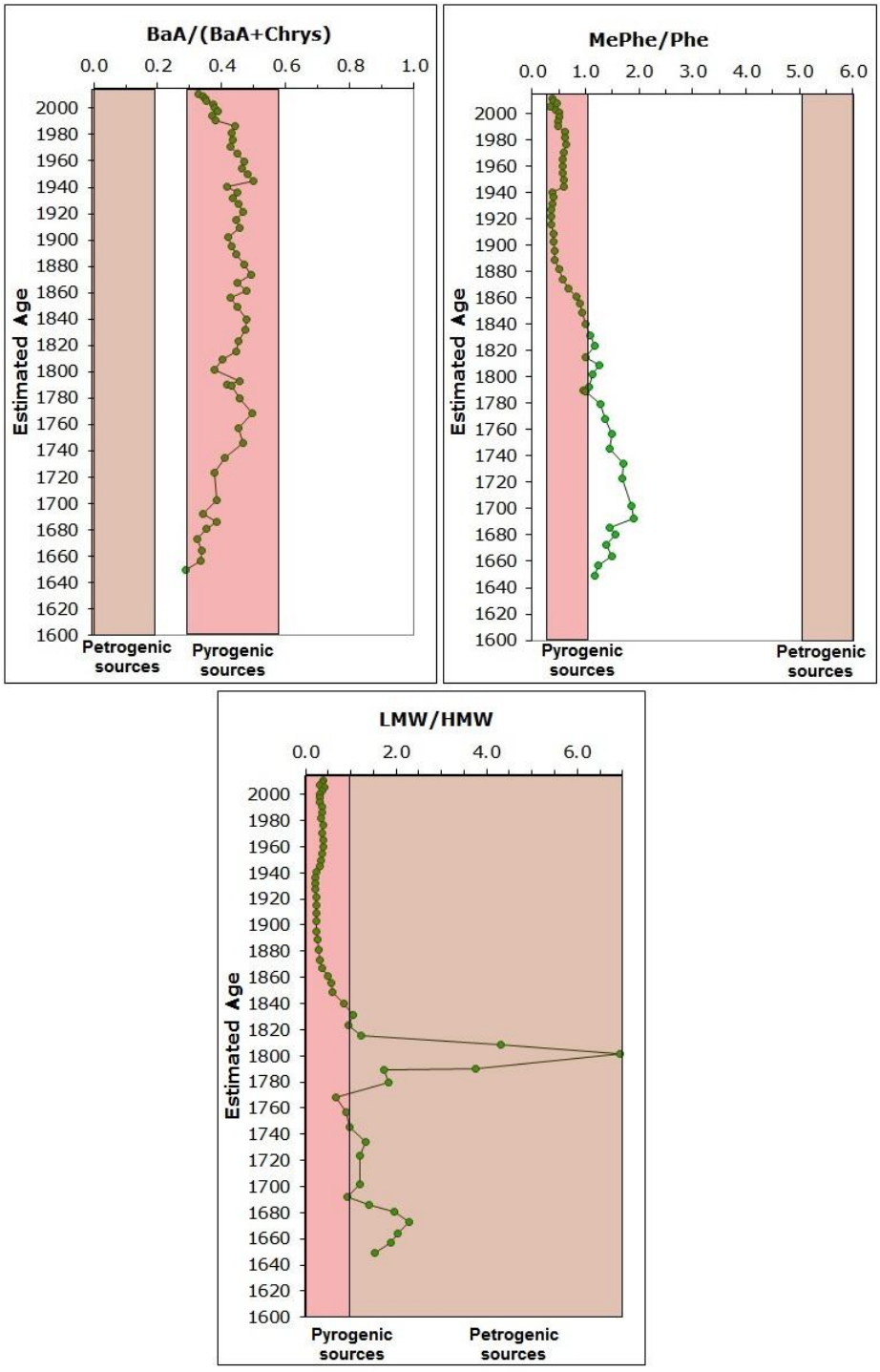

Figure A-1. Diagnostic ratios indicative of pyrogenic versus petrogenic sources. From top left to bottom, BaA/(BaA+Chrys), MePhe/(MePhe+Phe), and LMW/HMW PAHs.

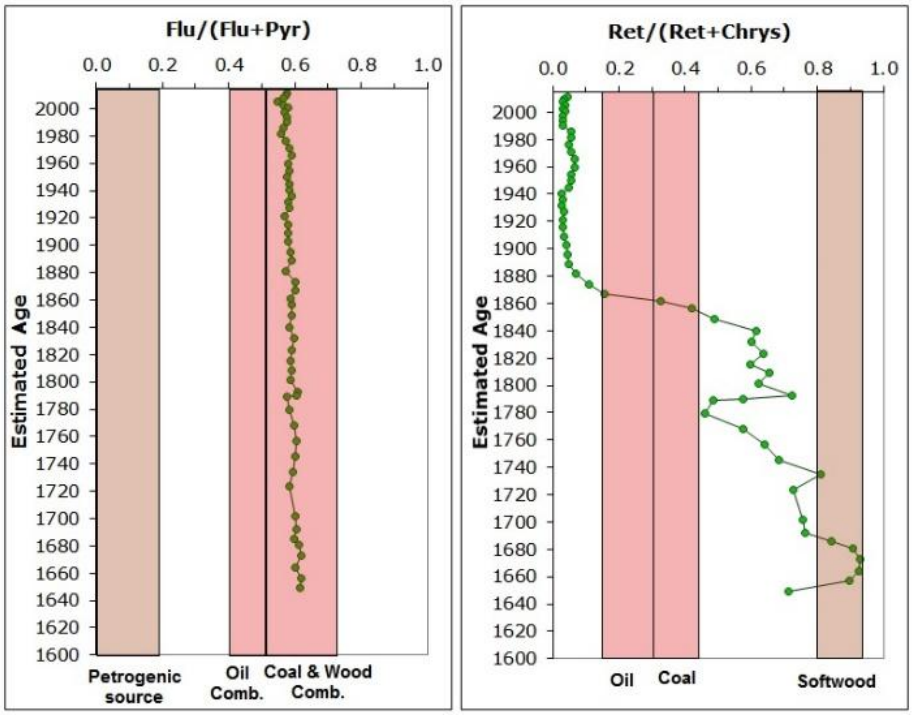

Figure A-2. PAH diagnostic ratios indicative of specific sources such as oil, coal, and wood combustion. Flu/(Flu + Pyr) (left) and Ret/(Ret + Chrys) (right).

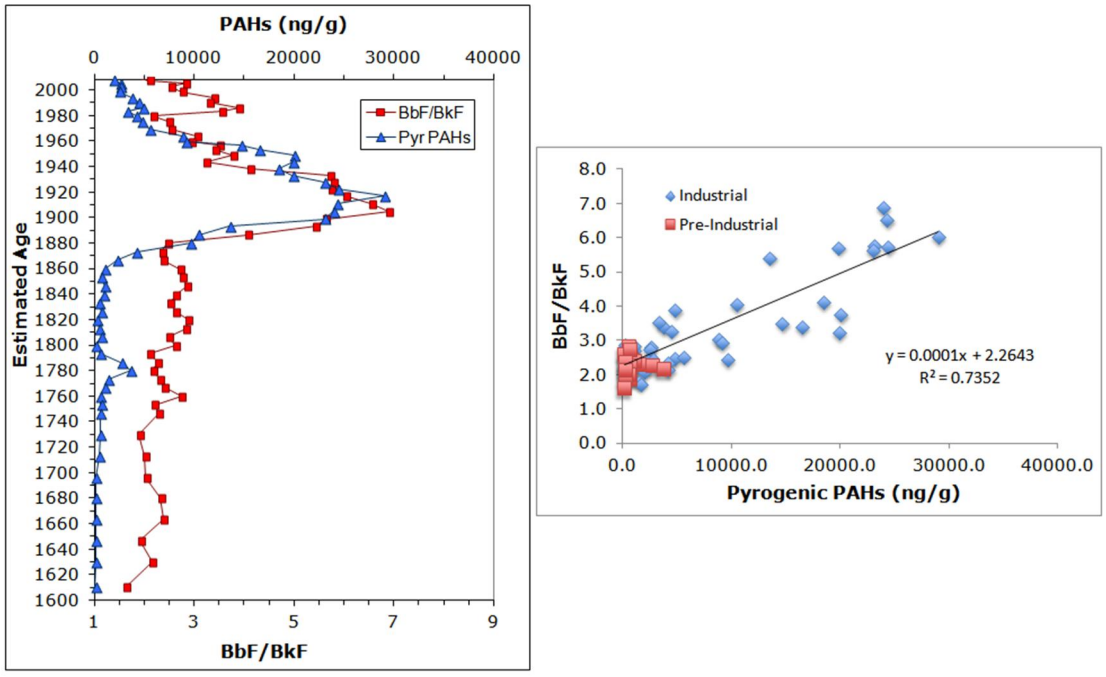

Figure A-3. Pyrogenic PAHs plotted against the ratio of BbF/BkF. The correlation between increasing concentrations of BbF/BkF and pyrogenic PAH emissions is depicted to the right.

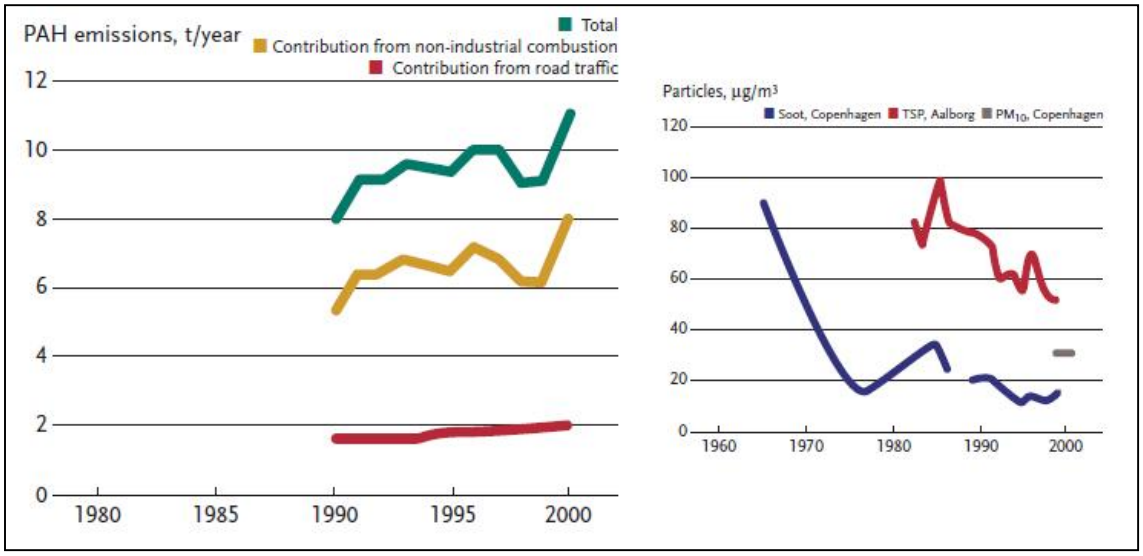

Figure A-4. PAH emissions in Copenhagen in recent years. The first graph (left) demonstrates the increases in four PAHs (BaP, BbF, BkF, and IP) while the second graph represents (right) the lowered PM emissions measured in a busy street in Copenhagen. Both studies were conducted by the National Environmental Research Institute and reported by Fenger (2003).

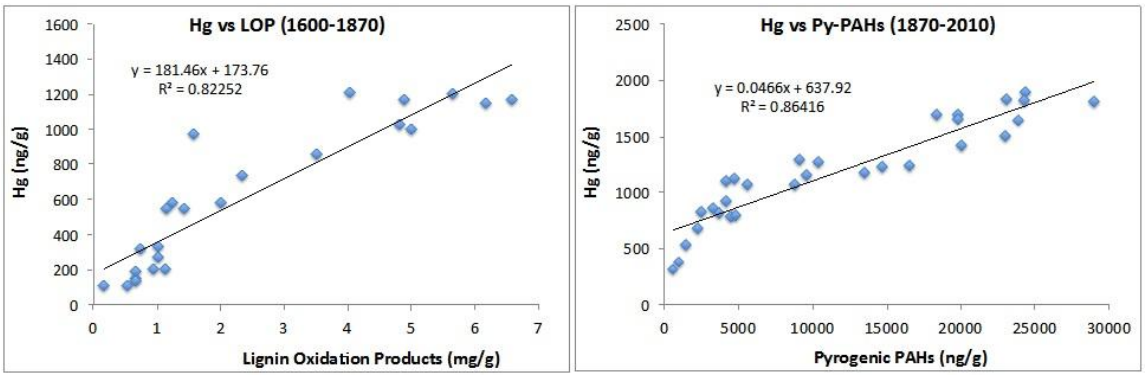

Figure A-5. Correlation of Hg and lignin in Lake Botanisk. The first graph (left) depicts the correlation between the years 1600 and 1870 indicates that during this time Hg inputs to the lake were likely due to greater inputs of organic matter to which Hg could be bound. The correlation of Hg and PyrPAHs (right) between the years 1870 and 2010 indicate that the primary input of Hg is decouple from lignin and is more strongly related to combustion-related atmospheric deposition.